# COORDINATION CHEMISTRY STUDIES OF BOND VALENCE SUMS OF SEVERAL METAL COMPLEX ENVIRONMENTS AND NICKEL (II) 2-ACETYLPYRIDINE THIOSEMICARBAZONES

By

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When I arrived in Gainesville in August 1995, I truly learned to live on my own as an adult. I had never lived an effective distance away from my parents for more than three months. I have lived in Gainesville longer than in any other location, except my hometown of Newburgh, Indiana. Coming from a different region of the United States and from a very small university (the University of Evansville has an enrollment of approximately 2400) sent my life into a different and enriching direction. I hope that I have made a positive contribution to the Department of Chemistry and the University of Florida.

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# TABLE OF CONTENTS

page

ACKNOWLEDGMENTS ........ ii

LIST OF TABLES ........ vi

LIST OF FIGURES ........ viii

ABSTRACT ........ ix

CHAPTERS

1 BACKGROUND AND INTRODUCTION ........ 1

Bond Valence Sum Studies ........ 1
Thiosemicarbazone Complexes ........ 7

2 POTASSIUM AND SODIUM COMPLEXES WITH OXYGEN DONORS ........ 9

Experimental Section ........ 10
Results and Discussion ........ 17
K-O Complexes ........ 17
Na-O Complexes ........ 27

3 COBALT COMPLEXES WITH OXYGEN DONORS ........ 39

Experimental Section ........ 39
Results and Discussion ........ 44

4 CHROMIUM COMPLEXES WITH OXYGEN DONORS ........ 52

Experimental Section ........ 52
Results and Discussion for Cr-O Complexes ........ 57

5 POTASSIUM AND SODIUM COMPLEXES WITH OXYGEN AND NITROGEN DONORS ........ 65

Experimental Section ........ 66

Results and Discussion ........ 72
K-O,N Complexes........ 72
Na-O,N Complexes........ 78

6 NICKEL (II) 2-ACETYLPYRIDINE THIOSEMICARBAZONES........84

Ni (II) di-(2-acetylpyridine thiosemicarbazone)........ 84
Ni (II) mono-(2-Acetylpyridine thiosemicarbazone)........ 88

APPENDICES

A LIST OF K-O,N COMPLEXES USED FOR THE BVS ANALYSIS........90

B LIST OF NA-O,N COMPLEXES USED FOR THE BVS ANALYSIS........99

C FORTRAN LINE CODING FOR PROGRAM USED IN CHAPTER 5........108

D TABLES OF CRYSTALLOGRAPHIC DATA........118

LIST OF REFERENCES........129

BIOGRAPHICAL SKETCH........143

# LIST OF TABLES

Table Page

2-1. The experimental values of $R_0$ (in Å) for K-O bonds as a function of the coordination number of the K atom ....13

2-2. The experimental values of $R_0$ (in Å) for Na-O bonds as a function of the coordination number of the Na atom ....14

2-3. Summary of K-O distances (in Å) used in the analysis ....15

2-4. Summary of Na-O distances (in Å) used in the analysis ....16

2-5. Summary of structural data for $KO_n$ complexes with some organic anions. ....23

2-6. Summary of structural data and BVS for K(18-crown-6)$^+$ complexes with various anions. ....24

2-7. Summary of structural data for $NaO_n$ complexes with some organic anions. ....32

2-8. Summary of structural data and BVS for $Na^+$ complexes with various anions. ....34

2-9. Summary of structural data and BVS for some Na(15-crown-5)$^+$ complexes with various anions. ....36

3-1. The values of $R_0$ (in Å) for Co-O bonds for oxidation states +2 and +3 ....41

3-2. The experimental values of $R_0$ (in Å) for Co-O bonds as a function of the coordination number of the Co atom. ....42

4-1. The values of $R_0$ for Cr-O bonds for oxidation states. ....54

4-2. Experimental values of $R_0$ for Cr-O Bonds (in Å) as a Function of Oxidation State and Coordination Number ....55

4-3. Summary of Cr-O Distances Used in the Analysis. ....56

5-1. Summary of BVS calculations for various K complexes with O and N donors. ....68

5-2. Summary of BVS calculations for various Na complexes with O and N donors. ....69

5-4. Summary of the distances used in the Na-O,N analysis. ........................................71

5-5. K-O,N complexes with K-$C_{(ring)}$ interactions..........................................................74

5-7. Na-O,N complexes with Na-C interactions. ..........................................................80

A-1. A listing of the BVS for the 238 $KO_nN_m$ (n = 0-6, m = 1-7) complexes used in the determination of K-N $R_0$ of 2.105 Å.........................................................................90

A-2. A listing of the BVS for the 33 $KO_nN_m$ complexes which were not used in the determination of K-N $R_0$ of 2.105 Å.........................................................................97

B-1. A listing of the BVS for the 242 $NaO_nN_m$ (n = 0-6, m = 1-7) ..................................99

B-2. A listing of the BVS for the 26 $NaO_nN_m$ complexes not used in the determination of Na-N $R_0$ of 1.935 Å. ..........................................................................106

C-1. Line coding for FORTRAN program used in Chapter 5. ........................................108

D-1. Crystallographic data for Ni(2-acetylpyridine thiosemicarbazone$)_2$ ........................118

D-2. Bond lengths [Å] and angles [°] for Ni(2-acetylpyridine thiosemicarbazone$)_2$.........120

D-3. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for Ni(2-acetylpyridine thiosemicarbazone$)_2$. ........................................122

D-4. Anisotropic displacement parameters ($Å^2$x $10^3$)for Ni(2-acetylpyridine thiosemicarbazone$)_2$. ..........................................................................125

D-5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for Ni(2-acetylpyridine thiosemicarbazone$)_2$..........................................................127

# LIST OF FIGURES

Figure Page

1-1. The thiosemicarbazone ligand. ........................................................................8

4-1. ORTEP drawing of $K_3Cr(O_2)_4$. ........................................................................62

6-1. ORTEP drawing for Ni (II) di-(2-acetylpyrdine thiosemicarbazone) dinitrate .........87

6-2. Suggested structure for Ni (II) mono-(2-acetylpyridine thiosemicarbazone) from reference 175. ........................................................................89

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# COORDINATION CHEMISTRY STUDIES OF BOND VALENCE SUMS OF SEVERAL METAL COMPLEX ENVIRONMENTS AND NICKEL (II) 2-ACETYLPYRIDINE THIOSEMICARBAZONES

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This dissertation deals with two areas of coordination chemistry: bond valence sums (BVS) studies and nickel (II) 2-acetylpyridine thiosemicarbazones. The BVS studies focus on six types of metal complex environments. These are M-$O_n$ (M = Na, K, Co, Cr; n = 3 – 8) and $NaO_aN_b$ and $KO_aN_b$ (a = 0 – 7, b = 1 – 8) complexes. For the Na-O environment, the $R_0$ value was determined at 1.756 Å. The $R_0$ value can be viewed as a length of unit valence. For K-O, it was 2.113 Å. For the Co-O, Cr-O, Na-N (determined from the NaON group), and K-N (determined from KON) interactions the values were 1.661, 1.724, 1.935, and 2.105 Å respectively. These $R_0$ values were found to reliably calculate the correct metal oxidation state for each of these complex types. For the cases of cobalt and chromium the $R_0$ values determined were oxidation state-independent. For the sodium and potassium environments, a novel covalent π-type interaction with the cations and the delocalized clouds of anionic organic rings was discovered. Also for the sodium and potassium sets, the BVS results offered an explanation for the differences between gas and solution stabilities for alkali-metal crown ether complexes. For each different cation environment various coordination complexes where the calculated BVS is much different from the expected are examined for possible reasons to explain the discrepancy.

2-Acetylpyridine thiosemicarbazones have therapeutic properties. Upon complexation, these properties sometimes increase in effect. Some reported nickel (II) $N^4$-substituted 2-acetylpyridine thiosemicarbazones have biocidal properties against various bacteria and other disease-causing agents. In contrast, the exploration into complexes of transitional metal $N^4$-unsubstituted-2-acetylpyridine thiosemicarbazones has been relatively scarce. This dissertation deals with the synthesis and medicinal testing of nickel (II) $N^4$-unsubstituted 2-acetylpyrdine thiosemicarbazone complexes.

# CHAPTER 1
# BACKGROUND AND INTRODUCTION

## Bond Valence Sum Studies

The bond valence sum (henceforth referred to as BVS) discussed in this dissertation derives from the simple notion of the correlation of a bond length and its bond strength. Unfortunately this notion has received a muddled treatment resulting in an unclear definition. To understand the evolution of BVS, a brief history is given here. The concept of the BVS can be traced back to Pauling.[1] In the study of the factors determining ionic crystal structure, he recognized in stable inorganic crystals the relationship between the radius ratio (the ratio of cation to anion radii) and coordination number. Pauling postulated that the number of polyhedra with a common vertex could be determined by the utilization of an extended conception of electrostatic valence.[1] Thus, Pauling defined electrostatic bond strength going to each corner of the polyhedron of anions about it as for ionic crystals as

$$s_{ij} = z_i / v_{ij} \qquad (1)$$

where $z_j$ is the charge or valence of the cation and $v_{ij}$ is the coordination number of atom *i* with respect to atom *j*. Equation (1) also works for cations as well. With this Pauling postulated that "in a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner" (1, p.1017). Thus for each anion:

$$\zeta = \Sigma s_{ij} = \Sigma\, z_j/v_{ij} \qquad (2)$$

where $z_j$ is the valence of atom *j* connecting *i-j* bonds with all neighboring i atoms and $\zeta$ is cation charge and the absolute value of anion charge. Hence for metal complex structures the oxidation state of the cation is the same as the valence. This equation is useful and straightforward if the coordination polyhedron around atom *i* is regular and the valences (or formal oxidation states) could be immediately determined from stoichiometry and the position of the element in the periodic table. One of the advantages of this method is the simplicity of interpreting results. While Pauling conceded that some crystals might not rigorously satisfy Equation (2), he anticipated many would yield good results. For example, a lithium oxide compound where the coordination around the lithium was 4 would have 4 Li-O bonds with electrostatic bond strengths of ¼ each. The four bonds would add up to give $\Sigma s_{ij} = 1$ for the lithium ion. The oxygen ions of that compound each would have a $\Sigma s_{ij} = 2$ value. Other examples include fluorine ions which would have $\Sigma s_{ij} = 1$ and Ti(IV) which would have $\Sigma s_{ij} = 4$. This new and powerfully useful electrostatic principle would be built upon in the development of the bond valence sum.

When the coordination configuration is irregular or the valence states of the atoms are unknown, an alternative equation is needed. Pauling--believing that metallic bonds were very similar to covalent ones (in disagreement with other investigators at the time)--proposed an option to Equation (1) where a relation between bond length *R* and bond strength--in this case the number of shared electron pairs or bond order *n*--is shown.

Since coordination chemical empirical information was lacking, he observed this type of dependence in a non-crystal chemistry source, the chemistry of carbon compounds. The length of a C-C single bond is 1.544 Å. For a double bond C=C the length is 1.330 Å. The difference between the single and double bonds, $\Delta R_1$, is –0.214 Å. The length of a triple bond C≡C is 1.204 Å and the difference between single and triple bonds, $\Delta R_2$, is -0.340 Å. The value of $\Delta R_1/\Delta R_2$ is equal to 0.629, nearly the same value as (log 2)/(log 3) which is equal to 0.630. Thus, he proposed that a bond-type correction might be taken proportional to the logarithm of the bond number, $n$

$$-\Delta R(n) = R(1) - R(n) = 0.353 \log n \qquad (3)$$

where $R(n)$ and $R(1)$ are carbon atom radii for an $n$th-bond and a single bond respectively in Å, and $n$ is the number of shared electron pairs involved in the bond, in Å. The value of 0.353, known now as parameter $b$, was determined by substituting the carbon atom radii of the different carbon-carbon bond values listed previously. However, a correction for the stabilizing or bond-shortening effect of resonance energy was needed. Pauling noticed that the value for the calculated interatomic distance of benzene ($n = 1.5$), 1.418 Å, was different from the actual value of 1.40 Å. Thus using Equation (4) for resonance correction

$$-\Delta R(\text{resonance}) = (A/v) \log \{N!/(\,v!\,(N-v)!)\} \qquad (4)$$

where $A$ is approximately 0.04 or 0.05, $v$ is the number of single bonds resonating among $N$ positions. Pauling incorporated the resonance correction in Equation (3) by reducing the $b$ parameter to a value of 0.300. With this equation, he obtained a nearly complete set of single-bond radii ($R_1$) for the elements. These $R_1$ values are looked upon as the atomic radii for a single bond of a cation-oxygen environment, equivalent to 1 unit of valence.

In comparison with "normal" covalent radii, tetrahedral radii, and octahedral radii, the single-bond values matched up similarly, supporting the idea that metallic bonding was "due to covalent bonds resonating among the available interatomic positions."[2] Hence, metallic bonding was very similar to the covalent type. Equation (3) could be successfully used with non-metal covalent compounds, metallic ones or metal complexes. With this new tool, a set of atomic radii was tabulated which one could use to evaluate the bond lengths of a given structure or calculate the interatomic distances in metal and intermetallic compounds.

For organic compounds the atomic valence is usually equal or greater than the coordination number, i.e. $n \geq 1$. Conversely though, for inorganic crystal compounds and metals the opposite usually composes the majority of cases. Thus, dealing with coordination compounds it is preferable and simpler to use the term bond strength $s$ instead of bond order $n$. There have been a variety of terms used to apply for bond strength, however, leading to some confusion. Zachariasen proposed the term "valence strength,"[3] Donnay and Donnay used the term "bond valence,"[4] while Pyatenko used "valence strength of a bond."[5] While all these terms can be used to describe parameter $s$, the most commonly accepted terms are "bond valence" (BV) or "bond valence sum" (BVS). The contemporary experts in this field commonly use these terms. Hence, these terms will be used to describe bond strength in this work.

Pauling's equation related bond strength to bond length by a factor of $1/v$. Others though improved on this by using analytical expressions, $R$-$s$ curves, to relate the relationship. Such $R$-$s$ curves were made from using the equations

$$s = s_i(R_{\mathrm{avg}}/R)^{\mathrm{p}} \quad \text{for } R \leq R_{\mathrm{avg}} \tag{5}$$

$$s = s_i((R_{\text{max}}\text{-}R)/(R_{\text{max}} - R))^{\text{p}} \quad \text{for } R_{\text{avg}} \leq R \leq R_{\text{max}} \qquad (6)$$

where $s_i$ is ideal bond strength of a bond length $R_{\text{avg}}$,[*] $s$ is bond strength of bond length $R$, and $R_{\text{max}}$ is largest cation-anion distance that still is considered a bond.[6,#]

There were several forms for the new bond strength-bond length expressions. One such expression of this by Bystrom and Wilhemi[7] used

$$R = R_1 - 2k \log s \qquad (7)$$

where $2k$ is equivalent to parameter $b$. A more commonly used expression

$$s_{ij} = (R_{ij}/R_1)^{-\text{N}} \qquad (8)$$

has $R_1$ and N as adjustable parameters. The parameter N represented several different things. Pyatenko[5] described the value of N as function of electronegativity where N increased with the electronegativity of the cation, or in effect N has an inverse relationship with cation size. Brown and Shannon[8] described N as a function of the number of core electrons. Allmann[9] described N as a function of size where for most elements $0.75<2k<1.1$ Å leads to a value of

$$\text{N} \sim 2.6\text{R}_{(\text{avg})} \qquad (9)$$

where $\text{R}_{(\text{avg})}$ is the average cation-oxygen length. Hence, N varies directly to cation size. Brown and Wu described N as a function of coordination number v

$$\text{N} \cong (0.6\,\text{v} + 2.2) \qquad (10)$$

where v is the coordination number for the cations.

With the increasing numbers of inorganic crystal compounds, the value of parameter $b$ was determined to be 0.37 Å[10] from a group of over 15000 various cation environments taken from the Inorganic Crystal Structure Database.[11] Thus the form of the equation describing bond valence took

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[*] The term $R$ in equations 3 and 4 refers to atomic radius; in the other equations it refers to bond length.

[#] In reference 6 valence is used instead of bond strength. However, I decided to retain Pauling's bond strength term to minimize confusion with competing terms.

$$R_{ij} = R_1 - b \ln (s_{ij}) \qquad (11)$$

where $b$ was regarded as a "universal" constant suitable for just about any type of atom. Bond strength $s$ was substituted for bond order $n$. Instead of having to decide from a multitude of different radii--covalent, tetrahedral, ionic, metallic, univalent, etc.--one could use the $R$ bond valence parameter value to estimate an unknown bond length for an ionic or non-ionic compound. Equation (11) was used to calculate the BVS values for the work discussed in this dissertation.

Both Equations (8) and (11) give similar results. But Equation (11) has an advantage due to the "universal" parameter $b$. Brown and Altermatt[10] found that $b$ varied little from one atom pair to another, thus enabling it to be used with impunity. For Equation (8) the parameter N must have different values substituted for it for different atoms. For Equation (11) that is not necessary. The BVS work done in our group utilizes the equations

$$z_j = \Sigma s_{ij} \qquad (12)$$

$$s_{ij} = \exp[(R_0 - R_{ij})/b] \qquad (13)$$

where $b = 0.37$ Å and $R_0$ is a parameter dependent on the nature of the metal-donor atom bond. (Equation (13) is the same as Equation (11)). These two equations have been successfully used by Palenik[12,13,14] to determine new $R_0$ parameters for the metal-ligand bonds of manganese with oxygen atom donors (Mn-O),[12] titanium with oxygen (Ti-O),[13] nitrogen (Ti-N),[13] and chlorine atom (Ti-Cl) donors,[13] and iron with oxygen atom donors (Fe-O).[14] The $R_0$ values for their cation-ligand environments are all oxidation state-independent; previous $R_0$ values for Mn-O, Ti-O, Ti-N, Ti-Cl, and Fe-O consisted of separate values for individual oxidation states and no single one that could be used to represent all oxidation states for a cation. Thus the equations could be used as a simple tool in determining the oxidation state of a cation without any assumptions. With the new oxidation state-independent values, any calculated BVS values that differed significantly from the expected indicated a number of different possible problems with the structure: incorrectly assigned oxidation states, misidentified cations, unnoticed or unreported interactions, or poor crystal quality. Thus, the new $R_0$ values can be used in coordination chemistry to evaluate various compounds in a simple, systematic manner.

The BVS work that is covered in this dissertation deals with the cation environments of sodium with oxygen or nitrogen donor atoms, potassium with oxygen or nitrogen donors, chromium with oxygen donors, and cobalt with oxygen donors. In these cases new and improved $R_0$ values (many previous $R_0$ values were calculated from ionic radii) are found and various interesting chemical applications for the BVS are discussed.

## Thiosemicarbazone Complexes

This dissertation deals with attempts at synthesis and characterization of biological activity of complexes of unsubstituted mono- and di-2-acetylpyridine thiosemicarbazones of nickel (II).

The thiosemicarbazone ligand (Figure 1-1) was synthesized from the reaction of thiosemicarbazide and a ketone or an aldehyde. Several structures in a series of 2-acetylpyridine thiosemicarbazones possess a significant antimalarial activity.[15,16] The biocidal activity of these compounds appear to be enhanced when the thiosemicarbazone molecule is complexed to a transition metal cation.[17] This is preferable since lower concentrations of the complexed ligand can exhibit the same or greater level of cytotoxicity than for higher concentrations of free ligand. Thus transition metal 2-acetylpyridine thiosemicarbazones are also a source of possible biological activity against many diseases. Various Ni(II),[18] Cu(II),[19] Mn(II),[20] and Fe(III)[21] metal complexes of $N^4$-disubstituted 2-acetylpyridine thiosemicarbazones have been prepared.

Complexes of nickel (II) 2-acetylpyridine thiosemicarbazones with unsubstituted $N^4$ atoms have been relatively unexplored in contrast to $N^4$-substituted nickel (II) 2-acetylpyridine thiosemicarbazones. Therefore, this dissertation covers efforts with the $N^4$-unsubstituted nickel (II) 2-acetylpyridine thiosemicarbazones.

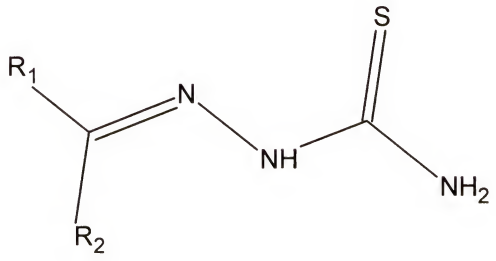

Figure 1-1. The thiosemicarbazone ligand.

# CHAPTER 2
# POTASSIUM AND SODIUM COMPLEXES WITH OXYGEN DONORS

The BVS studies of potassium with oxygen donors (henceforth K-O), K-$O_n$ (n = 3-9), and sodium with oxygen donors (henceforth Na-O), Na-$O_m$ (m = 3-8), gave new insights on the chemistry of potassium-oxygen and sodium-oxygen structures. As will be explained shortly, a novel type of interaction between both potassium or sodium cations and organic anions was discovered. Also, an explanation of the gas and solution/solid state stabilities of potassium 18-crown-6 ethers and sodium 15-crown-5 ethers, based on our BVS results, is provided.

The studies of the K-O and Na-O complexes were undertaken for several reasons. There is only one oxidation state and no complications occur from high and low spin configurations. Therefore, the K-O and Na-O complexes should have provided a good example of the effect, if any, of the coordination number on the BVS calculation, together with a clearer picture of the consequences of a non integer BVS.

Discussions of the K-O/Na-O distances and the coordination around the $Na^+$/$K^+$ ions are usually not given although that data can provide information regarding the correctness of the structure determination. One reason for the absence of a discussion of distances in K-O/Na-O complexes may be the lack of a recent compilation of K-O/Na-O distances to which reported structures can be compared. Therefore, as part of the analysis of K-O/Na-O complexes, various K-O/Na-O distances were tabulated as a function of coordination numbers that could then be used in a discussion of K-O/Na-O bond lengths.

The new $R_0$ values used in a BVS will hopefully be used in routine calculations for potassium and sodium compounds.

## Experimental Section

K-O and Na-O complexes. The bond length data for both the Na-O and K-O complexes were obtained from the April 1998 release of the Cambridge Structural Database (henceforth referred to as CSD) containing 181309 entries.[22] Those entries containing only O atoms coordinated to either K or Na were retrieved. For both potassium and sodium, the entries consist of the forms $NaO_n$ and $KO_m$ where n or m (n=3-8; m=3-9) is the number of oxygen donor atoms and also the total coordination number (henceforth referred to as CN). For K, a total of 196 entries in the CSD gave a starting set of 221 $KO_n$ complexes[23] after the duplicate entries were removed. For Na, a total of 327 entries in the CSD gave a starting set of 389 $NaO_n$ complexes[24] after duplicate entries were eliminated. A BVS for each entry was calculated using an initial $R_0$ value of 1.743 Å[25] for Na-O and 2.154 Å[26] for K-O in Equation (13).

After the BVS was calculated using the initial $R_0$ of 2.154 Å, for the potassium set, obvious erroneous or duplicate entries were removed or corrected at this point (individual corrections or removals are discussed in the Results and Discussion section). Then, an $R_0$ value, which minimized the sum of the squares of the differences between the reported and calculated oxidation states, was determined for each CN. The $R_0$ values determined for CN 3 through 9 are given in Table 2-1. There does not appear to be any trend in the values as a function of coordination number. The $R_0$ value that gave a BVS equal to 1 (the oxidation state for K) also was determined for each entry and these results are summarized in Table 2-3. For a given coordination number, there is no significant difference in the $R_0$ values determined in these two ways.

A complete listing of the BVS calculated for all of the $KO_n$ data for n = 3-9 using the $R_0$ value of 2.113(57) Å is available from the author or Dr. Gus J. Palenik or from the Internet.[23] A tabulation of the K-O bond length data as a function of coordination numbers is given in Table 2-3.

For the sodium set, the majority of the $NaO_3$ entries gave a BVS much less than 1.0 and was obviously erroneous. Inspection of the reports for these CN=3 complexes' reports revealed that some structures were polymeric in nature and had been classified incorrectly in the CSD.[*] In addition, some of the $NaO_3$ fragments appeared to form additional bonds to other groups, *vide infra*, and therefore were not included in subsequent calculations. For each coordination number, except CN=3, an $R_0$ value was determined for each entry so that the BVS was equal to the oxidation state, 1. Those individual $R_0$ values that differed by more than 2 sigma from the mean $R_0$ value were deleted, and a new mean and sigma were calculated. These results are summarized in Table 2-2. The final $R_0$ value of 1.756(42) Å was obtained by considering all coordination numbers from four to eight. The resulting set of 301 entries had no $R_0$ value differing by more than 2 sigma from the mean value, and the sigma for the calculated oxidation state was 0.11 valence units.

A complete listing of the BVS calculated for 389 $NaO_n$ complexes (n = 3-8) using the $R_0$ value of 1.756(42) Å may be obtained from the author or Dr. Gus J. Palenik or from the Internet.[24] A tabulation of the Na-O bond length data as a function of coordination number is given in Table 2-4. The BVS for both sodium and potassium sets were calculated using FORTRAN programs written by Dr. Gus J. Palenik.[*]

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[*] These and other corrections noted in this dissertation have been sent to the CSD and will be or have been included in a later release of the file.

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[*] Copies of the FORTRAN programs can be obtained from Dr. Gus J. Palenik.

Table 2-1. The experimental values of $R_0$ (in Å) for K-O bonds as a function of the coordination number of the K atom

| CN | no | $R_0$[a] | $R_0$[b] |
|---|---|---|---|
| 3 | 2 | 2.242 | 2.243(11) |
| 4 | 5 | 2.134 | 2.136(29) |
| 5 | 9 | 2.160 | 2.167(43) |
| 6 | 89 | 2.127 | 2.135(45) |
| 7 | 33 | 2.082 | 2.090(48) |
| 8 | 35 | 2.051 | 2.058(44) |
| 9 | 3 | 2.068 | 2.069(16) |
| 3-9 | 176 | 2.100 | 2.113(57) |

Note: CN is the coordination number and no is the number of complexes used for that CN.

a The $R_0$ value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states.

b The average $R_0$ value that makes the observed and calculated oxidation states equal, with the estimated standard deviation in parentheses.

Table 2-2. The experimental values of $R_0$ (in Å) for Na-O bonds as a function of the coordination number of the Na atom

| CN | no. | $R_0$ |
|---|---|---|
| 4 | 44 | 1.786(20) |
| 5 | 82 | 1.794(57) |
| 6 | 83 | 1.726(22) |
| 7 | 39 | 1.754(39) |
| 8 | 51 | 1.756(56) |
| 4-8 | 301 | 1.756(42) |

Note: CN is the coordination number, no. is the number of complexes used for that CN, and $R_0$ is the average $R_0$ value that gives a BVS equal to the oxidation state for each entry, with the estimated standard deviation in parentheses .

Table 2-3. Summary of K-O distances (in Å) used in the analysis

| CN | no | min | max | avg(sigma) | val |
|---|---|---|---|---|---|
| 3 | 6 | 2.591 | 2.742 | 2.654(68) | 0.232 |
| 4 | 20 | 2.568 | 2.824 | 2.653(59) | 0.232 |
| 5 | 45 | 2.636 | 2.958 | 2.769(82) | 0.170 |
| 6 | 534 | 2.536 | 3.137 | 2.801(69) | 0.156 |
| 7 | 231 | 2.461 | 3.089 | 2.819(90) | 0.148 |
| 8 | 280 | 2.604 | 3.168 | 2.835(86) | 0.142 |
| 9 | 27 | 2.675 | 3.098 | 2.892(93) | 0.122 |

Note: CN is the coordination number, no is the number of bonds found, min is the minimum K-O distance, max is the maximum K-O distance, avg is the average K-O distance, sigma is the standard deviation of the average value for the given CN, and val is the bond valence associated with a single K-O bond for a particular coordination number.

Table 2-4. Summary of Na-O distances (in Å) used in the analysis

| CN | no. | min | max | avg(sig) | val |
|---|---|---|---|---|---|
| 4 | 180 | 1.914 | 2.558 | 2.299(74) | 0.230 |
| 5 | 310 | 2.129 | 2.679 | 2.368(75) | 0.191 |
| 6 | 648 | 2.130 | 2.978 | 2.415(94) | 0.168 |
| 7 | 266 | 2.250 | 2.915 | 2.485(111) | 0.139 |
| 8 | 384 | 2.240 | 2.991 | 2.540(137) | 0.120 |

Note: CN is the coordination number, no. is the number of bonds found, min is the minimum Na-O distance, max is the maximum Na-O distance, avg is the average Na-O distance, sig is the standard deviation of the average value for the given CN, and val is the valence calculated for the average distance using Equation (13) with $R_0 = 1.756$ Å.

# Results and Discussion

## K-O Complexes

A new $R_0$ value of 2.113(57) Å for K-O bonds was determined from 176 K-O complexes with a CN of 3 through 9. This value is slightly but probably not significantly different from the reported values of 2.132(4) Å[26] and 2.13 Å[27] determined from only ionic solids or from the calculated value of 2.154 Å.[28] The agreement between these values is important since the data used to calculate the $R_0$ values are different; we are attempting to answer the important question of the validity of the BVS in coordination complexes. The lower estimated standard deviations on the previously reported values are probably due to the more uniform sample used to calculate these values. The small variation of $R_0$ with coordination number and possible interactions that have been missed will contribute to the larger esd of our value. An extra significant figure was retained for comparison purposes and in keeping with common crystallographic practices. Since the use of the BVS with coordination complexes is relatively new, the question as to the tolerated percent error is still under investigation. Therefore, an upper limit of 30%--0.3 valence units--was chosen. Some of the 10 entries that were not used in the determination of $R_0$ and the 16 complexes where the BVS differed by more than 0.3 of a valence unit from 1 are discussed. The discussion can be conveniently divided into two categories: those complexes where the BVS was much larger than 1.0 and those where the value was 0.7 or lower.

A BVS much greater than one for a KO complex can indicate an inappropriate cation, immense thermal motions, and/or problems with the crystal structure determination. This report provides examples for all of these situations. The complex TOSPUM[29,*]--containing a $K(THF)^+$ cation--had a BVS determined to be 2.71. The synthesis involved both $K^+$ and $Na^+$ salts. There was a lack of both an analysis and supporting evidence for the formulation of the product as the $K^+$ salt. Furthermore, the U(eq) of 77 for K was larger than that of the coordinated O atoms (57 to 73). Finally, the average K-O distance of 2.40 Å seemed very short, more in line with typical Na-O bond lengths. In comparison with other $K(THF)_6^+$ complexes, the authors noted that the $K(THF)_6^+$ species had been observed only once before--in the complex WADGOX.[30] For WADGOX the K-O distances averaged 2.741 Å and the BVS was 1.07. The $K(THF)_6^+$ complex TOPDIL,[31] a slightly later report which appeared at roughly the same time as the report for TOSPUM, the $K(THF)_6^+$ was reported with K-O distances averaging 2.698(30) Å and a BVS of 1.20, in reasonable agreement with the expected value. On account of the shorter than usual bond lengths and the mention of sodium salts used in the synthesis, TOSPUM was looked at as having a cation of $Na(THF)_6^+$; thus we would use the $R_0$ value for $Na^+$-O interactions of 1.743 Å.[23] Using that particular $R_0$ value we determined a BVS of 1.06 for TOSPUM. Therefore, we felt there was strong evidence that in TOSPUM the cation was really $Na(THF)_6^+$ instead of $K(THF)_6^+$ and that the entry should not be used in the K-O analysis.

Another structure that gave a large BVS was SEGSOM10.[32] The BVS for SEGSOM10 was calculated to be 2.93. While the *R* value of 0.066 appeared reasonable

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[*] Complexes downloaded from the Cambridge Structural Database (CSD) are referred to by their six-letter, uppercase code names. Some of the names in this dissertation also have two numbers at the end.

because of the relatively large three Re and seven Br atoms in the cell, the errors for the light atoms--carbon, nitrogen, and oxygen--were very great. The K-O distances were not well determined, with errors of ±0.03 Å. There were several possibilities for SEGSOM10's large BVS. The poorly defined K-O distances, the large thermal motion in the K-O bonds ($B_{isoeq}$ for O was 8(2)), and the fact that $Na^+$ introduced into the product (the BVS was 1.10 assuming $Na^+$ was the cation instead of $K^+$), were all qualified candidates for explaining the anomalous BVS result. Although we could not pinpoint with overwhelming clarity which reason caused the high value we decided to exclude these data.

A similar but somewhat more complicated case is that of TACGEJ, [33] where the BVS was 1.74. As with TOSPUM the synthesis was carried out using both $Na^+$ and $K^+$ salts. The main evidence for the formulation was given as the listed 5.2/1 excess of $K^+/Na^+$ and a Au, Br, C, H, and N analysis. However, substituting Na for K produced only a 1% change in the formula weight and only small changes in the calculated analysis. The space group was not determined uniquely from the systematic absences; the space group was determined to be one of three possible choices: *R32*, *R3m*, or *R-3m*. The reported structure solution seemed inordinately complicated for a compound in which the Au and K positions were fixed by symmetry considerations. In the final structure there was a 3-fold disorder in the $AuBr^{4-}$ anions, and the authors noted that the K-O distance of 2.56 Å appeared to be "much shorter" (31, p.248) versus other $KO_6$ coordination octahedral complexes. A simple substitution of $Na^+$ for $K^+$ is probably not the answer since the resulting BVS would be calculated to be roughly at a low 0.6-0.7.

Because there are so many questions concerning the structure determination the complex was not included in the analysis.

The BVS of 2.83 for KUHYOB[34] was one of the largest calculated for K-O complexes. KUHYOB, a rare nine-coordinate KO complex, was the unexpected product from the reaction of 18-crown-6 in $CH_2Cl_2$ with $K_2$tartrate·$0.5H_2O$ in $CHCl_3$. The chlorine found in the chemical analysis most likely arose from the hydrolysis of the $CHCl_3$. There is, however, a very "unusual asymmetric conformation of the [18-crown-6] crown ether ring around the $K^+$" (34, p.5165). Thus, the K-O distances are shorter than that of a majority of other 18-crown-6 complexes. The reasons for this strange conformation are not clear. One may regard the complex KUHYOB as a rare type of 18-crown-6 potassium complex in which the K-O distances lie on one end of the extreme from normal values. In a case like this the $R_0$ value poorly applies to the determination of the BVS. Thus this structure was not used.

For PIHXUZ[35] the BVS was 1.73, but the crystallographic *R* value of 0.106 was relatively high by current standards. The corresponding $Na^+$ and $Rb^+$ salts also were prepared. The main question is whether the $Na^+$ salt could have been used in the determination. One of the authors of the report stated that a refinement replacing $K^+$ with $Na^+$ gave unrealistically small thermal parameters. Unfortunately we could not evaluate whether the large BVS reflects large thermal motion since a thermal ellipsoid illustration was not shown in the report. However, the large BVS and high *R* value precluded using this data in our $R_0$ determination.

KO complexes with covalent interactions with organic anions. We have seen complexes in which various problems led to a BVS calculation of much greater than 1.0.

Conversely, in many cases a BVS much less than 1 usually indicates a missing interaction in the CSD file which may have been missed in the original report or may not have been included in the CSD entry. In the study of KO complexes we have come across what appears to be a novel type of interaction between $K^+$ ions and the $\pi$-molecular orbitals of anionic aromatic carbon rings. Several K-diglyme structures illustrate this point very nicely. For the K-diglyme complexes of KIXXIY[36] and KIXXUK,[37] the $K(diglyme)^+$ group is oriented toward a $C_8H_8^{2-}$ ring. The BVS are 0.51 and 0.49 respectively for the K-O interactions. Using a simple computer program called "Valence,"* it was calculated that 3 C atoms would contribute 0.36 or 0.30 to the BVS of KIXXIY and KIXXUK respectively. Thus the new BVS were determined as 0.87 and 0.79 for KIXXIY and KIXXUK respectively. The new values including the K-C interactions are much closer to the expected 1.0 and also give a CN of 6 around the $K^+$ ion. Assuming four bonds from K to the ring would give a BVS even closer to 1. These results suggest an interaction between the $K^+$ ion and pi orbitals of the $C_8H_8^{2-}$ ring. A comparison with a more traditional $K(diglyme)^+$ complex ZUHZOR[38], a $KO_7$ type complex with a BVS of 1.11, exhibited no particular problems or reasons for a K(diglyme) complex to not have a BVS of 1. Thus, KIXXIY and KIXXUK should be expected to have BVS values of 1 as well; hence, the argument of a covalent type bond between the K ion and aromatic rings in KIXXIY and KIXXUK is supported. A survey of other $K(O\ donor)^+$ complexes with these new interactions with a $C_8H_8^{2-}$ ring gave several examples. These are summarized in Table 2-5. These complexes were not included in the determination of the K-O $R_0$ because of their K-C interactions. All the complexes listed in Table 2-5 (CUBHIQ,[39] DULBER,[40] GILMET,[41] JITSOU,[42] KECOCE,[43] KIXXIY,[36] KIXXUK,[37] TIMQOV,[44] TMOCKE,[45] and ZESREU[46]) have K-C interactions where the potassium coordinates with a $C_8H_8^{2-}$ ring. For example, the complex CUBHIQ had a BVS of 0.46 using only the three O's coordinated to the $K^+$ ion. However, adding the contribution of 3 C's from the $C_8H_8^{2-}$ ring increased the value to 1.06 for a six-coordinate complex. If the contribution was 4 C's then the BVS was calculated at 1.26 for a seven-coordinate complex. The complex TIMQOV was a slightly different case. While there was a $C_8H_8^{2-}$ ring there was also a $C_5$ ring and an allyl group that contributed to the valence. In TIMQOV there is only one O coordinated to the $K^+$ ion, from a benzyl group, which gives a valence of only 0.21. Examination of the report showed that the $K^+$ ion was coordinated to the three different organic groups. Two carbon bonds to the $C_8$ group, three to the $C_5$, and two to the allyl group were used to calculate that the BVS would be 1.03. The question of whether the final CN for the complex should be 6 or 7 is unclear, but by viewing the data in Table 2-5, in either case the BVS is closer to the expected value. In summary, the BVS calculation provides clear evidence for a covalent type bond between the $K^+$ ion and the pi orbitals of organic ions, an interaction which apparently has not been proposed previously.[47,*]

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* This program is described in this reference: Brown, I. D. *J. Appl. Cryst.* **1996**, *29*, 479-480.

K(18-crown-6) ethers. Another group of complexes, those featuring K(18-crown-6)$^+$ cations, also had initial BVS values of much less than 1.0 The fact that a BVS less than 1 usually indicates missing interactions is well-illustrated by these various K(18-crown-6)$^+$ complexes. Table 2-6 features a collection of some of the structural data for complexes involving the K(18-crown-6)$^+$ cation and various anions. All of the

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[*] Reference 47 also contains a review of structural data on the organic compounds of alkali metals.

Table 2-5. Summary of structural data for $KO_n$ complexes with some organic anions.

| REFCODE | n | K-O val | K-Cavg | K-C val | BVS-6 | BVS-7 |
|---|---|---|---|---|---|---|
| CUBHIQ[39] | 3 | 0.46 | 3.017 | 0.20 | 1.06 | 1.24 |
| DULBER[40] | 4 | 0.49 | 3.14 | 0.14 | 0.77 | 0.91 |
| GILMET[41] | 2 | 0.28 | 2.957 | 0.23 | 1.20 | 1.43 |
|  | 3 | 0.65 | 2.986 | 0.22 | 1.21 | 1.43 |
| JITSOU[42] | 4 | 0.82 | 3.20 | 0.12 | 1.06 | 1.04 |
| KECOCE[43] | 3 | 0.53 | 3.16 | 0.14 | 0.95 | 1.09 |
| KIXXIY[36] | 3 | 0.52 | 3.191 | 0.12 | 0.88 | 1.00 |
| KIXXUK[37] | 3 | 0.50 | 3.263 | 0.10 | 0.80 | 0.90 |
| TIMQOV[44] | 1 | 0.21 | 3.145 | 0.14 |  |  |
|  |  |  | 3.174 | 0.13 |  |  |
|  |  |  | 3.342 | 0.08 |  | 0.96[a] |
| TMOCKE[45] | 3 | 0.46 | 3.003 | 0.21 | 1.09 | 1.30 |
| ZESREU[46] | 3 | 0.61 | 3.006 | 0.20 | 1.21 | 1.41 |

Note: REFCODE is the code used in the CSD file, n is the number of O atoms bonded to K, K-O val is the valence sum for the O donors, K-Cavg is the average K-C distance (in Å), K-C val is the valence of the K-Cavg distances using $R_0$ = 2.419 Å for the K-C bond, BVS-6 is the BVS assuming a coordination number of 6 for K achieved by forming 6-n K-C bonds, and BVS-7 is the BVS assuming a coordination number of 7 for K achieved by forming 7-n K-C bonds.

[a] Calculated by assuming 2 bonds to the $C_8$, 3 bonds to the $C_5$, and 1 bond to the benzyl group.

Table 2-6. Summary of structural data and BVS for K(18-crown-6)$^+$ complexes with various anions.

| REFCODE | BVS K-O | X,K-X | X,K-X | val | BVS |
|---|---|---|---|---|---|
| JOMDUK[48] | 0.83 | F,2.882 | F,2.661 | 0.25 | 1.08 |
| JOMFAS[49] | 0.81 | F,2.846 | F,2.653 | 0.27 | 1.08 |
| JOMFEW[50] | 0.82 | F,2.902 | F,2.622 | 0.26 | 1.08 |
| JOMFIA[51] | 0.81 | F,2.984 | F,2.596 | 0.26 | 1.07 |
| JOMFOG[52] | 0.76 | F,2.760 | F,2.731 | 0.26 | 1.02 |
| JOMFUM[53] | 0.77 | F,2.512 |  | 0.24 | 1.01 |
| SEYBUT10[54] | 0.70 | F,2.780 | F,3.042 | 0.18 |  |
|  |  | F,3.073 |  | 0.05 | 0.93 |
| KEGXID[55] | 0.92 |  | Cl,3.225 | 0.15 | 1.07 |
| FEHGEE[56] | 0.72 | I,3.856 | I,3.904 |  | 0.14 |
|  |  | I,4.105 |  | 0.04 | 0.90 |
| ZILXUN10[57] | 0.92 | Se,3.59 | Se,3.54 | 0.21 |  |
|  |  | Se,3.65 |  | 0.08 | 1.21 |

Note: REFCODE is the code used in the CSD file, BVS K-O is the valence sum for the O donors, X,K-X is the K-X distance (in Å) to the atom X, val is the sum of the valence contribution of the K-X bonds, BVS is the sum of both BVS K-O and val and is the final valence taking into account all the K$^+$ interactions.

complexes in Table 2-6 (JOMDUK,[48] JOMFAS,[49] JOMFEW,[50] JOMFIA,[51] JOMFOG,[52] JOMFUM,[53] SEYBUT10,[54] KEGXID,[55] FEHGEE,[56] and ZILXUN10[57]) have BVS values consistently much lower than 1. The examination of the reports of those structures, however, showed additional interactions of the type K-X where X was an atom that was not oxygen. We see that the BVS is less than 1 if we consider only the 6 oxygen atoms from the 18-crown-6; however, the K(18-crown-6)$^+$ interacts with the other negative centers to increase the CN and BVS. Unfortunately, in the case of K$^+$, these interactions are usually either not noted or not emphasized and may not be included in the CSD file. The extra interactions are all intermolecular and mostly with fluorine atoms, although chlorine, iodine, and selenium are also included. As seen in Table 2-6, addition of other K$^+$···anion interactions increases the BVS to the expected value. The empirical $R_0$ values[28] were used in the calculations so that the agreement is not as good as would be expected for carefully determined $R_0$ values. These results, however, can be used to explain the gas-phase versus solution stabilities of the K(18-crown-6) complexes.[58] In the gas phase the K$^+$ can coordinate only to the 18-crown-6 ether while in solution other interactions can occur. Thus, when examining this situation from a BVS point of view, in the gas phase, if the K$^+$ ion wants to achieve a BVS of 1 the crown ether must distort so then the K-O bonds constrict to give the desired result. In solution or solid state there is no need for the crown ether to distort since the extra interactions make up the missing BVS difference; the overall result is that the K$^+$ can achieve a BVS of 1 without undue distortions of the 18-crown-6 molecule. These results suggest that while the size of the 18-crown-6 cavity appears to be ideal for K$^+$ when one looks at the hard sphere radii, the electron distribution appears to be less than ideal for bonding to the K$^+$ ion. The knowledge of the suggestion that the electron distribution is important in the stability of crown ether complexes has indubitably not been suggested previously. A final note about the crown ether complexes: in the case of ZILXUN10[57] the compound was retrieved as a CN=3 structure and the initial BVS was only 0.45. In the original report the potassium cation was coordinated to the 18-crown-6 with six K-O interactions. However, only 3 of the 6 K-O bonds were recognized in the CSD entry. Addition of the three unrecognized K-O interactions increased the BVS to 0.92.

A summary of the K-O distances used in the analysis is given in Table 2-4. The average K-O distance increases from CN=3 to CN = 9 as expected. The average length is such that the valence contribution, calculated using Equation (13), multiplied by the CN is approximately 1.0 as required. Although the large difference between the minimum and maximum values is somewhat surprising, the result is not unexpected in view of previous results[12-14] and the requirement that the BVS = 1 for K-O complexes. The differing steric requirements of the ligands dictates some of the K-O distances, and the BVS can be satisfied by adjusting those bond distances which can be easily varied. The requirement that the BVS equal 1 is a more important condition than equality of the K-O distances. The large variation in the K-O distances also indicates the dangers in merely comparing K-O distances when discussing a K-O complex.

Conclusions for K-O complexes. For 195 $KO_n$ ($n = 3$–$9$) complexes the BVS calculated using Equation (13) with an $R_0$ value of 2.113(57) Å gives a value of 1 in most cases. When the BVS differs markedly from 1, there are usually problems with the crystal structure, misidentified cations, and unnoticed or unreported interactions. Therefore, one use of the BVS is confirmation of the crystal structure determination.

Equally or even more important, however, is the insight into chemical bonding provided by this simple calculation. We have shown that a pi-type interaction between $K^+$ and delocalized organic π-clouds is supported by the BVS calculations. In addition the BVS calculations can be used to explain the perplexing problem of the differences in gas phase versus solution stabilities of the alkali metal ions with various crown ethers. In summary the BVS is a simple calculation that can be used to understand the bonding in these complexes.

## Na-O Complexes

The $R_0$ value of 1.756(42) Å for Na-O bonds was derived from 301 NaO complexes with a CN of 4 through 8 by assuming that the oxidation state of Na was +1 and that Equations (12) and (13) were valid with b = 0.37 Å. The value is not significantly larger than an earlier value of 1.743 Å,[25] derived in a slightly different way, and is slightly but not significantly smaller than the values from ionic compounds(1.803 Å[26] or 1.80 Å[27]) and the empirical value of 1.80 Å.[28] The agreement between these values is important in establishing the validity of extending BVS from ionic solids to coordination complexes.

Since for 301 complexes the BVS equaled the oxidation state, the question arose as to the significance of the 88 cases where the BVS differed by more than 0.3 valence units or 2.7 sigma from one. A BVS differing from the oxidation state invariably indicated problems with the crystal structure report, such as an incorrect cation, additional interactions that were overlooked by the original authors or not included in the CSD file, or simply questions about the validity of the structure determination. Of the 88 entries that were not used in the determination of $R_0$ (in particular, those complexes where the BVS differed by more than 0.3 of a valence unit from 1.0) they can be conveniently divided into two categories: those complexes where the BVS was much larger than 1.0 and those where the value was much smaller than 1.0.

The complex VAXMUC[59] features two crystallographically different $Na^+$ ions with large BVS values of 2.26 and 2.32. Since there is no transition metal in the complex, the high BVS led to the suspicion that the cation was smaller than Na. Thus we operated on the assumption that the Na ions were actually Li. Examination of the report's experimental section showed that $LiPPh_2$ was used in the synthesis, thereby indicating an avenue where lithium could have been introduced. The Na-O distances ranged from 2.09 to 2.13 Å--all unusually shorter than expected and more in line with usual Li-O distances. It was decided to check what the BVS would be if the cations were lithium instead of sodium. By using the valence computer program where the $R_0$ for the Li-O bonds was set at 1.466 Å, the BVS was redetermined to be 1.02. That result suggests that the reported sodium ion was actually lithium. With lithium as the cation as opposed to sodium, the author's statement that "a rational synthesis" (59, p.221) did not yield the title compound could be explained. Because of these findings VAXMUC was not used in the analysis.

SULZEE10[60] had a BVS of 1.49. There were a number of questions about the structure determination. The complex is supposed to contain three sodium ions but only Na(1) was retrieved from the CSD file. Na(2) was disordered about the mirror plane. Na(3) was not retrieved on the assumption that the Na-O distances were all very long; the BVS for Na(3) was determined to be 0.253--a very small value. The isotropic temperature factors show that while Na(1) has a reasonable $U_{eq}$ value of 21(6), Na(2) and Na(3) have much higher--higher than most of the other atoms in the structure--values of

73(6) and 92(7) respectively. The bond lengths for Na-O also varied greatly. For Na(1) the Na-O lengths ranged from 2.259 to 2.296 Å. For Na(2) the range was 2.689 to 2.982 Å. For Na(3) the range was 2.625 to 2.991 Å. For Na(1), the lengths were shorter than usual while for Na(2) and Na(3) they were longer than usual. The synthesis of the complex involved a mole ratio of 12:10 for Na:K (6 moles of $Na_2MoO_4$:10 moles KCl). There is a possibility that the sodium could be partially substituted by potassium. If the cation was assumed to be potassium, then the calculated BVS is 0.67, closer to 1 than if assuming sodium. Another possible reason for high BVS values is large thermal parameters. For this example the report mentioned that some water molecules in the crystals "were smeared out due to large thermal parameters" (60, p.137). High thermal parameters can lead to bond lengths that appear shorter than they actually are, increasing the BVS. Another possible problem with this complex is that only about half the measured reflections--2162 out of 4215--were used, leading to a limited data set and possibly a poor refinement. Hence, for those reasons SULZEE10 was not used in the analysis.

Like SULZEE10, the complex YOVCOB[61] also had a BVS of 1.49. There is some doubt about the existence of the $Na^+$ ion in the structure. There is no chemical analysis given to support the formulation. Likewise, to the best of our knowledge, a full report has not appeared. The authors note "because of disorder it has not been possible to locate the anion and solvent units precisely and the *R* factor cannot be reduced below 0.0830" (61, p.459). The existence of the anion is critical to the formulation as a Na salt and the authors cite ". . .a very similar copper(II) analogue. . .$[Na\{Cu(mhp)_2\}_6]$[62]. . ." (61, p.461) in support of their structure. They also noted, however, that the source of the $Na^+$

in [Na{Cu(mhp)$_2$}$_6$] was unexplained. The compound [Na{Cu(mhp)$_2$}$_6$] was found in the CSD file as JODGAK.[62] This entry had not been retrieved in our search for Na-O complexes. For JODGAK the BVS of 1.54, calculated using the reported Na-O distance of 2.26 Å, is also too large. The authors of JODGAK's report stated "the presence of the central sodium ion is serendipitous" (62, p.1453). That statement is most likely accurate since the starting material was the potassium salt of 6-methyl-2-hydroxypydridine. The description of the synthesis of the structure is somewhat ambiguous since the authors do not mention when or where sodium is introduced into the reaction mixture. Also, the *R* factor is 0.0838, a large value like for YOVCOB. Despite the authors' contention that the central cation is sodium and not potassium, the preceding evidence supports a contrary view. In conclusion with respect to YOVCOB and JODGAK we feel that both structure reports should be viewed warily pending further data to support their formulations as sodium salts. Therefore, YOVCOB and JODGAK were not used in the analysis.

PEANNA[63] is a good example of the uses of the BVS. For this case the BVS is a reliable indicator of the correctness of a crystal structure determination. The Na-O distances in the report were very long (range: 2.713-3.167 Å for 8 different bonds), resulting in an extremely low BVS of 0.38. A subsequent new determination of the structure in PEANNA11[64] was classified as a five-coordinate structure in the CSD file with a BVS of 0.72. However, examination of the report[64] showed it to be eight-coordinate $Na^+$ with a BVS of 0.90. The two different CNs are probably due to the fact that three of the Na-O lengths were 2.949, 3.425, and 3.718 Å long. The authors were studying both $Na^+$ and $Ag^+$ complexes in PEANNA; it is feasible that the two cations were interchanged in some fashion, replacing $Na^+$ with $Ag^+$ for PEANNA. Using the valence program, a BVS of about 0.53 was calculated for the silver complex. Therefore, PEANNA was not used in the analysis.

Na complexes with covalent interactions with organic anions. When the BVS is much less than 1 this can indicate missing interactions that either have not been included in the CSD or were missed in the original report. PEZTET[65] is a good example of this problem. PEZTET was listed in the CSD with a coordination number of four; the BVS was calculated at 0.60. Examination of the report showed a figure of PEZTET where close to the Na ion was an aromatic $C_6H_6^-$ ring; for bond distances there was a Na-$C_b$ ($C_b$ is the centroid of the aromatic ring) value of 2.717(6) Å. Estimating the Na-C distance to be about 3.00 Å and using 2.079 Å for $R_0$ for Na-C bonds (by using the valence program), we obtained a BVS of 0.21 for three Na-C bonds. Added to the original BVS, this gives a new value of 0.81, closer to 1.0. Examination of the report showed that the authors mentioned a "significant interaction" between the sodium cation and the carbon ring. However, they did not discuss this in detail. The new BVS indicates that the carbon ring is donating electron density to the sodium cation in a novel covalent interaction. PEZTET was not used in the analysis since it did not fit the criterion of a complex with only oxygen donors for the sodium cation.

The result of PEZTET led us to search the CSD for other similar sodium compounds that have aromatic ring interactions. This inspection yielded the complexes LEPHAP,[66] ROQFEI,[67] and YICTAF[68] (Table 2-7). All of these complexes feature sodium ions with oxygen donors that appeared to be interacting with $C_8H_8^{2-}$ rings. For these structures the BVS is very low when the carbon ring interactions are not included in the calculation. When the extra interactions are included the BVS increases closer to 1.0.

Table 2-7. Summary of structural data for $NaO_n$ complexes with some organic anions.

| REFCODE | n | Na-O val | Na-Cavg | Na-C val | BVS-6 | BVS-7 |
|---|---|---|---|---|---|---|
| PEZTET[65] | 4 | 0.60 | 3.06 | 0.07 | 0.74 | 0.81 |
| LEPHAP[66] | 3 | 0.49 | 3.00 | 0.08 | 0.73 | 0.81 |
| ROQFEI[67] | 3 | 0.68 | 3.07 | 0.07 | 0.88 | 0.95 |
| YICTAF[68] | 3 | 0.71 | 2.94 | 0.09 | 0.98 | 1.07 |

Note: REFCODE is the code used in the CSD file, n is the number of O atoms coordinated to Na, Na-O val is the valence sum for the O donors, Na-Cavg is the average Na-C distance (in Å) , Na-C val is the valence of the Na-Cavg distances using $R_0 = 2.419$ Å for the Na-C bond, BVS-6 is the BVS assuming a coordination number of 6 for Na achieved by forming 6-n Na-C bonds, and BVS-7 is the BVS assuming a coordination number of 7 for Na achieved by forming 7-n Na-C bonds.

These results point to the suggestion that the carbon ring atoms show a markedly significant contribution to the overall BVS, thus indicating at least a partial covalent Na-C bond. Table 2-7 gives the BVS values for those complexes with Na-C interactions included. The complex HAHNUZ[69] appeared to have Na-C interactions as well, but a lack of information prevented a calculation of its new BVS; this entry was not used in the analysis. The BVS for both coordination numbers six and seven are included; the new actual coordination is unclear.

Na-O complexes with other secondary interactions. Several other complexes had other secondary interactions with the Na ion that were not noted or emphasized in the CSD. The additional interactions are not of the type of the sodium-aromatic ring variety as with LEPHAP or the other complexes with that type of coordination. One example, the complex FACGIZ,[70] was listed under CN=3 and had a BVS of 0.64. Examination of its report showed that there were two Na-N bonds of 2.766 and 2.757 Å. Using a $R_0$ of 1.891 Å,[25] the BVS contributions of the Na-N bonds were determined as 0.09 and 0.10 respectively. Added to the original BVS, these two contributions redetermined the BVS to be 0.93, a much closer value to the expected 1.0. Table 2-8 gives additional examples showing how other $Na^{+}\cdots X$ (X = electron-donor atom) interactions increase the BVS to the expected value of 1.0. The majority of these secondary interactions are of the Na-F type, but there are others that include donor atoms of N, Cl, I, and S. Also, the majority of the complexes were of the CN=3 variety, thus exhibiting the rarity of CN=3 sodium complexes with a sodium-oxygen-only environment. Besides the example of FACGIZ there were many other similar examples of structures[68-78] where extra interactions increased the BVS, shown in Table 2-8. The interaction of the $Na^{+}$ with anions has been postulated on the basis of infrared data;[81] our BVS calculations provide new evidence for this type of interaction.

Na (15-crown-5) ethers. Another group of Na-O complexes has extra secondary interactions as well. The case for this arises when the BVS is significantly lower than 1.0 and the complex features a $Na(15\text{-crown-}5)^{+}$ cation, a source of another interesting and chemically informative example. As with the previous examples and the potassium (18-crown-6) ether complexes, Table 2-9 shows that Na(15-crown-5) complexes also have extra interactions not shown nor emphasized in the BVS. Considering only the 5 Na-O interactions with the oxygen atoms of the 15-crown-5 ring, the BVS is usually much less than 1.0. When considering the extra interactions with the Na, the BVS rises closer to 1.0. These results can be used to explain the gas-phase versus solution stabilities of the

Table 2-8. Summary of structural data and BVS for $Na^+$ complexes with various anions.

| REFCODE | n | BVS Na-O | X,Na-X | X,Na-X | VAL | BVS |
|---|---|---|---|---|---|---|
| FACGIZ[70] | 3 | 0.64 | N,2.766 | N,2.757 | 0.19 | 0.83 |
| FEXBAL10[71] | 6 | 0.41 | N,3.115 | N,3.010 | 0.09 | 0.50 |
| FTPNTF10[72] | 3 | 0.64 | N,2.784 | N,2.825 | 0.17 | 0.81 |
| GABYAJ[73] | 3 | 0.64 | Cl,2.982 | Cl,2.913 | 0.27 | 0.91 |
| HAGYAP[74] | 3 | 0.69 | F,2.641 | F,2.831 | 0.12 | |
| | | | F,2.922 | F,3.009 | 0.06 | |
| | | | F,3.447 | F,2.365 | 0.16 | 1.03 |
| | | 0.76 | F,2.652 | F,2.993 | 0.10 | |
| | | | F,3.379 | F,3.750 | 0.01 | |
| | | | F,2.480 | F,2.993 | 0.14 | 1.01 |
| | | 0.70 | F,2.636 | F,2.635 | 0.15 | |
| | | | F,3.471 | F,2.411 | 0.15 | |
| | | | F,2.745 | F,3.640 | 0.06 | 1.06 |
| | | 0.64 | F,2.698 | F,2.736 | 0.12 | |
| | | | F,2.857 | F,3.337 | 0.05 | |
| | | | F,3.506 | F,2.805 | 0.05 | |
| | | | F,3.375 | | 0.01 | 0.87 |
| HILDAH[75] | 3 | 0.68 | I,3.301 | I,3.540 | 0.21 | |
| | | | I,3.209 | | 0.18 | 1.07 |
| KIGGAI[76] | 3 | 0.68 | S,3.00 | S,3.00 | 0.45 | |
| | | | S,3.00 | | | 1.13 |
| KIDSAR[77] | 4 | 0.57 | N,2.438 | | 0.23 | 0.80 |
| YOXTUA01[78] | 3 | 0.72 | F,2.621 | F,2.566 | 0.17 | |
| | | | F,2.503 | | 0.11 | 0.97 |
| | 3 | 0.74 | F,2.751 | F,2.486 | 0.16 | |

Table 2-8--continued.

| REFCODE | n | BVS Na-O | X,Na-X | X,Na-X | VAL | BVS |
|---|---|---|---|---|---|---|
| YOXTUA01[78] | | | F,2.514 | F,3.095 | 0.12 | 1.02 |
| YOXTUA01[78] | 3 | 0.69 | F,2.883 | F,2.805 | 0.09 | |
| | | | F,3.178 | F,2.736 | 0.07 | |
| | | | F,3.153 | F,3.323 | 0.03 | 0.88 |
| ZAQZII[79] | 3 | 0.65 | F,2.899 | F,2.774 | 0.09 | |
| | | | F,2.960 | F,3.637 | 0.04 | |
| | | | F,2.332 | F,3.746 | 0.17 | 0.97 |
| | 3 | 0.68 | F,2.635 | F,2.774 | 0.08 | 0.76 |
| ZAWMEP[80] | 3 | 0.54 | F,2.408 | F,2.621 | 0.22 | |
| | | | F,2.658 | F,2.521 | 0.17 | |
| | | | F,2.633 | | 0.08 | 1.01 |
| | 3 | 0.51 | F,2.520 | F,2.598 | 0.18 | |
| | | | F,2.489 | F,2.589 | 0.20 | |
| | | | F,2.857 | | 0.04 | 0.93 |

Note: REFCODE is the code used in the CSD file, n is the coordination of the sodium with oxygen atoms, BVS Na-O is the valence sum for the O donors, X,Na-X is the Na-X distance (in Å) to the atom X, VAL is the sum of the valence contribution of the Na-X bonds, and BVS is the sum of BVS Na-O and Val, and it is the final valence taking into account all the $Na^+$ interactions.

Table 2-9. Summary of structural data and BVS for some Na(15-crown-5)$^+$ complexes with various anions.

| REFCODE | n | BVS Na-O | X,Na-X | X,Na-X | VAL | BVS |
|---|---|---|---|---|---|---|
| JAVKAS[82] | 5 | 0.70 | F,2.402 | Cl,2.871 | 0.31 | 1.01 |
| | 5 | 0.78 | F,2.265 | Cl,3.189 | 0.27 | 1.05 |
| JAZGEW[83] | 5 | 0.68 | Cl,2.86 | Cl,2.85 | 0.35 | 1.01 |
| KIYKUY[84] | 5 | 0.75 | F,2.306 | F,2.332 | 0.35 | 1.10 |
| KIYLAF[85] | 5 | 0.73 | F,2.333 | F,2.293 | 0.36 | 1.09 |
| LEZDAV[86] | 5 | 0.79 | I,3.330 | | 0.18 | 0.97 |
| POTCOA10[87] | 5 | 0.63 | N,2.396 | S,2.287 | 0.34 | 0.97 |
| SAMZUB[88] | 5 | 0.54 | Se,2.981 | | 0.22 | 0.76 |
| SANBAK[89] | 5 | 0.67 | Se,2.978 | | 0.22 | 0.89 |
| SANBEO[90] | 5 | 0.75 | Se,3.00 | | 0.21 | 0.96 |
| TADFUZ[91] | 5 | 0.68 | Cl,2.768 | | 0.22 | 0.90 |
| | 5 | 0.76 | Cl,2.651 | | 0.30 | 1.06 |
| VOTCAI[92] | 5 | 0.50 | S,3.084 | S,3.082 | 0.23 | |
| | 5 | | S,3.334 | | 0.06 | 0.79 |
| WAHFAM[93] | 5 | 0.65 | F,2.418 | F,2.301 | 0.32 | 0.97 |

Note: REFCODE is the code used in the CSD file, n is the coordination of the sodium with oxygen atoms, BVS Na-O is the valence sum for the O donors, X,Na-X is the Na-X distance (in Å) to the atom X, VAL is the sum of the valence contribution of the Na-X bonds, and BVS is the sum of BVS Na-O and Val, and it is the final valence taking into account all the Na$^+$ interactions.

Na(15-crown-5) complexes, as shown in Maleknia and Brodbelt's report.[58] As shown in their report, $Li^+$, despite $Na^+$ having the ideal size for a 15-crown-5 ether cavity, is actually preferred for the gas-phase selectivity. The results are similar for the 18-crown-6 and 21-crown-7 ethers where the next smaller ion from the ideal one (on size basis alone) is preferred; for 18-crown-6 sodium is preferred while for 21-crown-7 rubidium is preferred. In the gas phase the $Na^+$ can only coordinate to the 15-crown-5 ether molecule; the 15-crown-5 ether must distort exceedingly for the $Na^+$ to achieve a BVS of 1.0, thus explaining the undesirability of selectivity in the gas phase. In solution or solid state this is not necessary since the $Na^+$ can interact with other atoms to achieve a BVS of 1.0. In conclusion, while the physical size of the 15-crown-5 cavity appears to be ideal for $Na^+$, the electronic distribution is not.

Distances in Na-O complexes. As seen in Table 2-4 the average Na-O distance increases with coordination numbers. As observed with other systems,[12-14] this is not unexpected. The use of the BVS model makes it simple to grasp the increase in the average distance. In Table 2-2, the valence calculated for the average distance is in agreement with the predicted bond valence of 1/CN if all the Na-O bonds are of equal length. Thus, as long as the BVS equals 1.0 then the Na ion will employ any combination of bond lengths. Since the BVS must be satisfied for all coordination numbers, the sum becomes a better indicator of structure correctness and quality than the usual $R$ value. The large variation in the Na-O distances for a given coordination number indicates the danger in merely comparing bond distances when discussing a Na-O complex.

Conclusions for Na-O complexes. For the 389 $NaO_n$ complexes the BVS calculated using Equation (13) with an $R_0$ value of 1.756(42) Å gives a value of 1 in most cases. When the BVS differs notably from 1, there are frequently problems with the crystal structure, misidentified cations, and unnoticed or unreported interactions. Therefore, an important use of the BVS is confirmation of the crystal structure determination. Perhaps even more important is the understanding of chemical bonding provided by this intelligible calculation. We have shown that a pi-type interaction between $Na^+$ and delocalized organic pi-clouds--usually from aromatic anionic ligands--is supported by the BVS calculations. In addition, the BVS calculations can be used to explain the perplexing problem of the differences in gas phase versus solution stabilities of the alkali metal ions with various crown ethers, in this case the question why a 15-crown-5 ether does not prefer a "perfect fit" $Na^+$. In summary, the BVS is a simple calculation that can be used to understand the bonding in these complexes as well as to avoid introducing errors into the literature.

# CHAPTER 3
# COBALT COMPLEXES WITH OXYGEN DONORS

The BVS study of cobalt complexes with solely oxygen donor atoms (henceforth Co-O) provided a different challenge from the sodium-oxygen and potassium-oxygen studies. Two oxidation states--+2 and +3--were present for cobalt, thus making necessary a $R_0$ value that would work well for both states. For the complexes where the Co-O $R_0$ value did not yield a desirable result, usually either an incorrect CN in the CSD or problems with the crystallographic quality were the reason for the much higher or lower BVS.

## Experimental Section

The June 1997 release of the Cambridge Structural Database (CSD)--167797 entries[22]--was used to obtain the bond length data of the Co-O complexes. For the coordination numbers of three through eight only those entries where there were only oxygen donor atoms for the cobalt cations, i.e. $CoO_n$ where $n = 3\text{-}8$, were used. There were 199 entries from the CSD to give a starting group of 227 $CoO_n$ complexes.[94] The $R_0$ value was set initially[28] at 1.680 Å in Equation (13). This value was used to determine an oxidation state for each individual entry. At this juncture, entries that were evidently incorrect were corrected or discarded (see Results and Discussion for details). Entries that were alike were removed. The next step involved determining a $R_0$ value that brought the sum of the squares of the differences between the reported and calculated oxidation states to a minimum for each different CN. This process was then conducted for the oxidation states of +2 and +3 individually and then for all the coordination numbers grouped together. The $R_0$ values for the CNs are presented in Table 3-2. The $R_0$ value declines as coordination increases from three to six. It then rises slightly as the coordination number increases to eight. The $R_0$ values for the oxidation states of 2 and 3 are shown in Table 3-1 in comparison to several previous literature values. The final $R_0$ of 1.661(16) Å was obtained from the average of the +2 and +3 oxidation state values.

The Co-O bond length data used for this investigation are presented in Table 3-3. The BVS was calculated utilizing FORTRAN programs authored by Dr. Gus J. Palenik.

Table 3-1. The values of $R_0$ (in Å) for Co-O bonds for oxidation states +2 and +3

| | Oxidation State of Co | |
|---|---|---|
| Reference | +2 | +3 |
| 26 | 1.692 | |
| 27 | 1.692 | 1.70 |
| 28 | 1.680 | 1.680 |
| WP | 1.685 | 1.637 |

Note: Equation (13) with b=0.37 was used in references 26, 27, and 28. WP are the results presented in this dissertation.

Table 3-2. The experimental values of $R_0$ (in Å) for Co-O bonds as a function of the coordination number of the Co atom.

| CN | No | $R_0$ |
|---|---|---|
| 3 | 4 | 1.748 |
| 4 | 22 | 1.704 |
| 5 | 6 | 1.686 |
| 6 | 190 | 1.670 |
| 7 | 5 | 1.684 |
| 8 | 1 | 1.695 |
| 5-8 | 226 | 1.754 |

Note: CN is the coordination number, No is the number of complexes used for that CN, and $R_0$ is the value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states.

Table 3-3. Summary of Co-O distances used in the Co-O analysis.

| Ox | CN | No | Min | Max | Avg(Sigma) | Val |
|---|---|---|---|---|---|---|
| 2 | 3 | 12 | 1.763 | 1.981 | 1.906(82) | 0.516 |
| 2 | 4 | 84 | 1.845 | 2.073 | 1.960(41) | 0.446 |
| 2 | 5 | 30 | 1.893 | 2.453 | 2.043(116) | 0.356 |
| 2 | 6 | 1002 | 1.874 | 2.450 | 2.093(56) | 0.311 |
| 2 | 7 | 28 | 2.018 | 2.251 | 2.152(60) | 0.265 |
| 2 | 8 | 8 | 2.033 | 2.538 | 2.260(217) | 0.198 |
| 3 | 6 | 132 | 1.866 | 2.168 | 1.895(30) | 0.531 |

Note: Ox is the oxidation state of Co, CN is the coordination number, No is the number of bonds found, Min is the minimum Co-O distance (in Å), Max is the maximum Co-O distance (in Å), Avg is the average Co-O distance (in Å), and sigma is the standard deviation of the average value for the given CN, Val is the valence calculated for the average distance using Equation (13) with $R_0 = 1.661$ Å.

## Results and Discussion

Co-O complexes. The BVS was determined for 227 $CoO_n$ complexes, where n = 3 to 8, using an initial $R_0$ value of 1.680 Å[28] and then a final $R_0$ of 1.661(16) Å. Several structures with deviant BVS values were examined closely for potential reasons for the wayward results. The following discussion elaborates in more detail about those entries.

There were several structures that apparently were not classified correctly in the CSD file in terms of CN. Two $CoO_3$ entries, GIRPUS[95] and JIJPIB,[96] both had a BVS of 0.98 rather than the expected 2.0. Examination of the reports for the two structures showed that both GIRPUS and JIJPIB had a polymeric structure in the solid state with $CoO_6$ coordination. Due to their polymeric nature GIRPUS and JIJPIB were not classified correctly in the CSD file, reflected by the very low BVS.* Hence, it was necessary that the two entries be removed from the $CoO_3$ set. The missing Co-O bonds were added to make the entries six-coordinate, and then the BVS for both were recalculated and attached to the $CoO_6$ set. The new BVS were determined as 1.82 and 1.83 for GIRPUS and JIJPIB respectively.

The complex TBACCO[97] was hard to evaluate due to the relative lack of facts and discussion of this structure. The BVS was 2.57 as opposed to the reported 2.0. An average Co-O bond length of 1.981 Å was given but no other bond information or any thermal parameter values were supplied. Since the crystallographic *R* value was given as 0.00 and a detailed report was not readily accessible, this entry was not included in subsequent calculations.

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* The CSD is working on the problem of polymeric compounds.

Often complexes that are listed as three-coordinate in the CSD exhibit BVS values that are much lower than the expected value. The BVS calculated using an $R_0$ of 1.661 Å for the two CN=3 complexes FIRSII[98] (BVS = 1.58 and 1.68) and FIRSOO[99] (BVS = 1.54 and 1.52) illustrate the difficulties with small CNs. Metal complexes with low CNs are usually synthesized by using very sterically bulky ligands. Under these circumstances, the bonds are unusually long which means the BVS is lower than expected. These complexes also are generally greatly reactive. Looking at these complexes from a BVS perspective, any reactions of these complexes usually increase the CN and would presumably yield a BVS closer to the proposed oxidation state. Thus for FIRSOO and FIRSII the low coordination is the reason for the lower than expected BVS. An example of this can be seen within the report; in the report it is seen that the addition of THF to FIRSOO results in a complex that has four-coordination around the Co cation, FIRTAB.[100] The BVS for FIRTAB, 1.81, is closer to the theoretical value of 2.00. There is a slight improvement for FISRII (BVS=1.69 and 1.79) and for FIRSOO (BVS=1.65 and 1.62) if the Co(II) $R_0$ value of 1.685 Å is used. Even for the Co(II) $R_0$ the BVS is low enough to indicate the problem of steric hindrance.

The anion--featuring three nitromalonaldehyde ligands coordinated to the cobalt--in the complex BAMNIM[101] is octahedral (BVS = 2.31). But the structure was refined using only isotropic thermal parameters to a relatively high crystallographic *R* value of 0.109, "... ignoring the contribution of seven reflections with large values of $|F_o - F_c|$..." (101, p.2863). The authors noted that attempts to refine the structure anisotropically gave unreasonable thermal parameters. Also, with the collection and reduction of x-ray data where despite a reasonable crystal size (0.21 x 0.26 x 0.48 mm) the crystal "diffracted weakly showing a significant fall-off of intensities at higher angles" (98, p.2863). And out of 5836 reflections only 1942 were considered " 'observed' having $I \geq \sigma(I)$" (100, p.2863). Thus, the structure was seen as unreliable and therefore not included.

For both HAZDOB10[102] (BVS = 2.36) and ZAXHIP[103] (BVS = 1.58), the cation is a radical tetrathiafulvalene derivative and the Co(II) is in a Keggin-type polyoxotungstate anion, $CoW_{12}O_{40}^{6-}$. In their report the authors note that the Keggin anions

> . . .appear as centrosymmetric units as a result of disorder due to a rotation of 90° around the $C_2$ axis of the central tetrahedron. This kind of disorder has been found in other crystal structures with Keggin anions surrounded by big and weakly polarizing cations. . .(102,103, p.4141).

A result of this disorder is ". . .the impossibility of refining all the oxygen atoms of the anion with anisotropic thermal parameters" (102,103, p.4141). Therefore, the Co-O bond lengths are not as accurate as needed: the large deviation of the BVS from 2.0 is not unexpected. These complexes were consequently not used.

COPTOX,[104] CN=6, is a one-dimensional paramagnetic conductor. The formula for COPTOX was $Co_{0.83}[Pt(C_2O_4)_2] \bullet 6H_2O$. The fractional occupancy of the Co(II) could account for the low BVS of 1.38 compared to an ideal value of 2. To support this postulate, COPTOX was compared with an isostructural magnesium complex, $Mg_{0.82}[Pt(C_2O_4)_2] \bullet 5.3H_2O$.[105] For this complex there are six Mg-O bonds of two of each length of 2.23, 2.13, and 2.23 Å. Using the valence program, the BVS contributions for those bonds were calculated at 0.268, 0.351, and 0.268 respectively to yield a total of 1.774. While not as low as the BVS for COPTOX the value is consistently on the low side, illustrating how fractional occupancy can affect the BVS.

The high crystallographic *R* value of 0.12--like BAMNIM's *R* value of 0.109--for the four-coordinate complex GLYCCO10[106] (BVS = 1.75) is a legitimate reason in itself to not employ this entry. However, on inspection of the original report it was found that the Co was five and not four coordinate as shown in the CSD. The addition of the fifth Co-O bond increased the BVS to 2.07, in agreement with the presence of Co(II) in the complex. For this complex, similar to what was conducted with GIRPUS and JIJPIB, the lower-coordination, CN=4, entry was removed and the new, corrected entry was placed in the CN=5 set.

Since the ions in PASFCO[107] and PASCON10[108] are very similar they are useful in illustrating an example of the use of the BVS in examining the coordination in metal complexes. The refinements of PASFCO and PASCON10--the crystallographic *R* values are 0.105 and 0.098 respectively--are not considered to be the quality of today's standards. However, a contrasting of the two is still informative and valid since in both cases we want to understand whether the CN is four or eight. For PASFCO, the ion $Co(CF_3COO)_4^{2-}$ has $D_{2d}$ symmetry. There are four Co-O lengths at 2.00 Å and four additional ones at 3.11 Å; there is one length of each associated with each trifluoroacetate ligand coordinated to cobalt. The ion was catalogued as 4-coordinate in the CSD. The BVS was determined as 1.62. Examination of figure 1 in the report[107] revealed that a drawing illustrating the structure had the length of 3.11 Å as not designated as a bond interaction. Addition of the four Co-O distances of 3.11 Å increased the BVS slightly to 1.68. PASCON10 was used in comparison since it possessed similar structure features. For PASCON10, the cation of $Co(NO_3)_4^{2-}$ had a coordination of eight and the symmetry is $C_2$. The Co-O distances are two of each length of 2.03, 2.11, 2.36 and 2.54 Å. The coordinated nitrate ligands had two Co-O lengths of either 2.03 and 2.36 Å or 2.11 and 2.54 Å. The BVS of PASCON10 was determined as 1.82. Like PASFCO, there are four Co-O lengths that are significantly shorter than the other four Co-O interactions. Figure 1 given in the report[108] confirmed the CN=8 state since all eight Co-O interactions were designated as bonds. If the BVS was calculated using only the 4 shorter Co-O interactions with an $R_0$ of 1.661 Å, a BVS of 1.33 would be obtained. With the BVS providing guidance, it is confirmed that PASCON10 is an eight-coordinate complex. Thus an eight-coordinate Co-O complex, where four Co-O bonds are noticeably shorter than the other four, can exist. Hence, it is entirely reasonable to reclassify PASFCO as an eight-coordinate complex instead of four. If the Co(II) $R_0$ value is used for PASFCO and PASCON10, the BVS is 1.81 and 1.94 respectively. These results suggest that both structures should be considered as eight-coordinate species. The fact that the BVS is slightly lower than the expected 2.0 may involve steric problems with the high CN (as noted on Table 3-2, the $R_0$ for CN = 8 is higher than for CN = 5-7) or the inferior crystallographic quality, reflected in the high *R* values for both entries.

The BVS was determined as 1.51 for the entry of VORTOL.[109] This value was one of the lowest for a Co(II) complex. VORTOL was one of the more interesting examples, for a variety of reasons, of the CoO set. There are several questions that point to the quality of the structure determination. The proportions of the crystal size appeared satisfactory--0.18 x 0.18 x 0.31 mm--but only about 1/3 of the unique reflections observed (1331 out of 3914) “were assumed as observed, applying the condition $I=3\sigma(I)$” (106, p.135). As we have seen, less than half of the reflections observed can indicate problems with the refinement. The hydrogen atoms were isotropically refined while the heavier non-hydrogen atoms were refined anisotropically; the ratio of observed reflections to variables thus ended up at about 5 or 6. In the report, figure 2[109] used only small spheres for the anisotropically refined atoms--the thermal parameters were not available. However, there was concern with the isotropic $B_{eq}$ values reported. Two different things about those values were quite strange. First, the accuracy of the $B_{eq}$ varied by a factor of about 2, with the Co and Na ions having larger estimated standard deviations than some of the lighter atoms. Second, the $Na^+$ $B_{eq}$ (9.34(2) Å$^2$) was much greater compared to those of the $Co^{2+}$ (4.18(3) Å$^2$) and the lighter (carbon, oxygen, nitrogen) atoms (3.0 to 6.0 Å$^2$). Finally, neither the values of the Na-O distances nor a detailed description of the coordination of the $Na^+$ ion was given. Using a simple FORTRAN program called PARST*, the parameters were retrieved from the CSD file and used to estimate all the intra- and interatomic lengths involving the Co and Na ions. The results suggest that the $Na^+$ appears to be 9 coordinate. However, all the Na-O bond lengths were much longer than usual. There were the distances of 3 Na-O lengths at 2.999 Å, 3 at 3.073 Å, and 3 at 3.290 Å. These are all too long for a significant contribution to the Na BVS. The BVS for the $Na^+$ ion is only 0.23--much smaller than the expected 1.0. In summary for the sodium ion, the results show that the $Na^+$ ion does not appear to be in contact with any other atom. Due to this questionable point and the others of VORTOL it was concluded that the crystal structure determination has serious flaws.

Conclusions for Co-O complexes. A summary of Co-O distances is included in Table 3-3. The Co-O distances used in the BVS analysis are shown as a function of oxidation state and CN. For oxidation state +2 the average Co-O distance increases with an increase in CN with the oxidation state holding constant which is expected. For the other oxidation state, Co(III), the data included only six-coordinate complexes. The average value for those is smaller than that of the corresponding CN of Co(II), as expected. A summary of the Co-O distances used in our analysis is given in Table 3-3. The average length is such that the valence contribution, calculated using Equation (13), multiplied by the CN yields an answer of approximately 2.0 as required. As for the sodium and potassium environments, the large range of bond distance values given in Table 3-3 illustrates an important point about the dangers of relying solely on comparisons of bond distances when examining a complex. The large variation in the Co-O distance for any given combination of oxidation state and CN is understandable in terms of the BVS. Ligand constraints can restrict the magnitude of Co-O distances that are possible: the other ligands must assume distances that are compatible with the BVS being equal to the oxidation state for that CN. The parameter of the BVS being equal to the oxidation state of the metal ion takes precedence over a constant bond radius. This parameter must be fulfilled, even at the cost of a constant bond radius. Under these conditions, the calculation of the BVS can be more important than bond distance comparisons or the usual crystallographic *R* value in assessing the accuracy of a crystal structure determination.

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* This program can be obtained from Dr. Gus J. Palenik.

The Co-O $R_0$ of 1.661 Å has been shown satisfactorily to be used to calculate the oxidation state of the Co atom in coordination complexes containing only Co-O bonds with no prior assumptions. The results are in agreement for oxidation states of Co(II) and Co(III) by using a simple calculation for the BVS. When there was a deviation of the BVS from an integer value, it usually indicated either possible steric constraints, excessive thermal motion, problems with the crystal structure report, or some combination of all of these effects. The examples included here illustrate these points.

# CHAPTER 4
# CHROMIUM COMPLEXES WITH OXYGEN DONORS

The study of chromium complexes with oxygen donors (henceforth Cr-O) examines the problems in establishing an oxidation state independent $R_0$ value for Cr complexes of different oxidation states with O donors. The Cr case was chosen because of the range of oxidation states--2, 3, 4, 5, and 6--and the different $R_0$ values, summarized in Table 4-1, that have been reported for Cr-O bonds in ionic solids.[26-28] One of the difficulties in determining an $R_0$ is the requirement for accurate bond length data; this can be obtained from crystal structure data provided the determination has been carried out properly. We have found that one of the best guides for assessing the accuracy of a structure determination has been the BVS. The use of structural data only from those compounds where the BVS agrees with the expected value has been the primary procedure. Thus, determination of the "best" $R_0$ value requires a careful assessment of the crystallographic data and of experimental details in those cases where there is a discrepancy between the calculated BVS and the postulated oxidation state.

## Experimental Section

The Cr-O bond length data was taken from the May 1999 release of the Cambridge Structural Database (CSD) containing 197481 entries.[22] Only entries containing O atoms coordinated to Cr were retrieved--i.e. $CrO_n$ (where n = (3 – 6, 8) and is the number of Os and also the coordination number (CN)). A total of 172 entries from the CSD gave a starting set of 242 $CrO_n$ complexes.[110] In addition, literature data for $K_3CrO_8$[111-113] were added, and new data for that complex, *vide infra*, were included. Table 4-1 shows the oxidation state-dependent $R_0$ values obtained from this study in comparison with previous literature values. An initial $R_0$ value of 1.737 Å[26] was used to calculate an oxidation state for each entry. Any obvious erroneous oxidation states were corrected at this point and any duplicate entries were removed. An $R_0$ value was determined for each entry so that the BVS was equal to the postulated oxidation state. Those $R_0$ values that differed by more than 2.5 $\sigma$ from the mean value were deleted; then a new $R_0$ value and $\sigma$ were calculated. The resulting $R_0$ values are given in Table 4-2. The $R_0$ determined in this way did not differ significantly from the $R_0$ value that minimized the sum of the squares of the differences between the reported and calculated oxidation states. An analysis of the Cr-O bond length data used with these results is given in Table 4-3. The BVS was calculated using FORTRAN programs written by Dr. Gus J. Palenik.

Table 4-1. The values of $R_0$ for Cr-O bonds for oxidation states.

| | Oxidation State of Cr | | | |
|---|---|---|---|---|
| Ref. | +2 | +3 | +5 | +6 |
| 26 | 1.724 | | | 1.794 |
| 27 | 1.730 | 1.724 | | 1.794 |
| 28 | 1.750 | 1.750 | 1.750 | 1.750 |
| WP | 1.739 | 1.708 | 1.762 | 1.793 |

Note: Equation (13) with $b = 0.37$ was used in references 26, 27, 28, and WP. WP is the dissertation work.

Table 4-2. Experimental values of $R_0$ for Cr-O Bonds (in Å) as a Function of Oxidation State and Coordination Number.

| | Oxidation State of Cr | | | |
|---|---|---|---|---|
| CN | +2 | +3 | +5 | +6 |
| 3 | 1.769(10) | | | |
| no. | 2 | | | |
| 4 | 1.735(23) | | | 1.793(7) |
| no. | 15 | | | 53 |
| 5 | 1.741(4) | | 1.770(8) | |
| no. | 4 | | 6 | |
| 6 | 1.735 | 1.708(7) | | |
| no. | 1 | 115 | | |
| 8 | | | 1.738(14) | |
| no. | | | 4 | |
| best | 1.739(21) | 1.708(7) | 1.762(14) | 1.793(7) |
| no. | 22 | 115 | 9 | 53 |

Note: Equation (13) with b = 0.37 was used for the $R_0$ determination. CN is the coordination number and no. is the number of entries used to determine the $R_0$ value. The estimated standard deviation where appropriate is given in parentheses after the value.

Table 4-3. Summary of Cr-O Distances Used in the Analysis.

| ox | CN | no. | min | max | avg(sigma) | val |
|---|---|---|---|---|---|---|
| 2 | 3 | 6 | 1.825 | 1.986 | 1.925(73) | 0.58 |
| 2 | 4 | 60 | 1.943 | 2.097 | 1.992(31) | 0.48 |
| 2 | 5 | 20 | 1.973 | 2.392 | 2.099(132) | 0.36 |
| 2 | 6 | 6 | 2.022 | 2.499 | 2.195(236) | 0.28 |
| 3 | 4 | 4 | 1.824 | 1.973 | 1.882(71) | 0.65 |
| 3 | 6 | 810 | 1.811 | 2.096 | 1.967(32) | 0.52 |
| 4 | 4 | 4 | 1.771 | 1.775 | 1.773(2) | 0.86 |
| 5 | 5 | 30 | 1.533 | 1.921 | 1.795(131) | 0.83 |
| 5 | 8 | 24 | 1.881 | 1.958 | 1.920(29) | 0.59 |
| 6 | 4 | 212 | 1.554 | 1.881 | 1.647(72) | 1.23 |

Note: Ox is the oxidation state, CN is the coordination number, no. is the number of bonds found, min is the minimum Cr-O distance (in Å) found for that oxidation state and coordination number, max is the maximum Cr-O distance (in Å) found for that oxidation state and coordination number, avg(sigma) is the average Cr-O distance (in Å) found for that oxidation state and coordination number, with the estimated standard deviation in parentheses, and val is the valence of the average distance using Equation (13) with $b = 0.37$ and $R_0 = 1.724$Å.

## Results and Discussion for Cr-O Complexes

Cr(II), Cr(III), and Cr(IV) complexes. The $R_0$ of 1.724 Å, the average of the Cr(II) and (III) $R_0$ values of 1.739 and 1.708 Å respectively, is satisfactory for the calculation of the oxidation state for the Cr ion without any assumptions. When 1.724 Å was used in Equation (13) for 163 Cr(II) and (III) complexes with CN = 3 – 6, only six examples were calculated with oxidation states that differed by more than 0.30 from the expected integer oxidation state value. The $R_0$ of 1.724 Å worked well also for our CN = 8, $K_3CrO_8$ structure; the calculated value was 4.74, close to the expected oxidation state of 5. However, for the oxidation states of +5 (complexes from the CSD file) and +6, where CN = 4 or 5, the agreement between calculated and theoretical oxidation state values is much worse. A discussion of these Cr(V) and Cr(VI) examples follows.

For complexes where steric constraints are prominent, the expected BVS can be or is calculated much lower than the expected value. Usually, we see this situation arise where CN = 3 and the ligands are made up of bulky groups such as t-butyl. Three examples in this Cr-O set illustrate the point. For CUSXET[114] (BVS = 1.82 and 1.86 for the two crystallographically independent Cr(II) atoms), LIBCRA[115] (BVS = 2.53), and LIBCRB[116] (BVS = 3.50) the values are all lower than expected; the expected values are 2.0 for CUSXET, 3.0 for LIBCRA, and 4.0 for LIBCRB. These low values are explicable because of steric constraints involving the bulky t-butoxide and t-butyl ligands that were needed to achieve a low coordination number. Furthermore, in the case of LIBCRA the authors noted "... the specimen finally chosen for the study was still of lower quality than would have been preferred" (114, p.1869) so that the quality of the data in this case may be less than optimum.

The BVS can be used to differentiate ligands that are members of a redox series. In the case of the two complexes CBZQCR[117] and TBZQCR,[118] the question to be answered is whether the ligand is a catecholate, semiquninone radical anion, or an unreduced *o*-benzosemiquinone. In both cases the ligand was assumed to be neutral and the Cr was assigned a 0-oxidation state. However, the BVS, using our average $R_0$ value, were determined as 3.27 for CBZQCR and 3.42 for TBZQCR. Thus, it appears that the Cr is +3 in both cases and that each ligand is -1. If the $R_0$ value for Cr(III) of 1.708 Å was used, the BVS is 3.13 for CBZQCR and 3.28 for TBZQCR, in even better agreement with the formulation as Cr(III) and a -1 ligand. The BVS is larger than expected in both cases, perhaps reflecting high thermal motion that tends to make the observed bond lengths shorter and the BVS larger. In the case of TBZQCR the authors state that "the weak packing forces result in large thermal motion of the tert-butyl groups" (118, p.235).

The chemistry of cluster complexes can be studied using the BVS. Here, it was used to confirm the assumptions regarding oxidation state and the identity of the metal ions in the cluster complexes. Several examples were found which contained $\mu_3$-oxo-$Cr_3$ clusters where the BVS around the Cr ions is very close to 3. For KOPNIM[119] the chromium ions have BVS values of 3.01, 2.98, and 3.02. For WABJUE[120] the BVS values are 2.97, 2.99, and 2.91. COVPOS,[121] a similar structure with a $Fe_2Cr$ core, the Cr BVS is 2.67, a slightly low value. The synthesis of COVPOS involved a 1:2:6 mixture of Cr(III) and Fe(III) perchlorates and glycine. The authors deduced that the $Fe_2Cr$ core was ordered by looking at the thermal parameters from the structural analysis. The BVS around the two Fe atoms was calculated at 3.02 and 3.00 (using an $R_0$ of 1.745 Å as determined in a previous study of FeO clusters)[14] that supported the postulation of an ordered structure. However, one difficulty with COVPOS was an ambiguity in the space group between *Cc* and *C2/c*. The authors used *Cc* without giving any justification for the choice and this may account for the deviation of the BVS from the expected value of 3.

PINFOH[122] is another cluster complex. However, in this case the BVS of 2.60 and 2.53 were in poor agreement with the expected values. In this complex there is a Mn(II) cation that is coordinated to three $Cr(ox)_3$ ions in a polymeric structure. There were several problems with this structure. There was a space group ambiguity with two possible choices, *R-3c* and *R3c*. The authors stated that "for good reasons the Patterson synthesis was started in the centrosymmetric space group *R-3c*" (122, p.66) but they did not elaborate. The authors did not discuss the assignment of the metal atom types and, in fact, the thermal ellipsoids looked very strange in the ORTEP drawing[122] of the structure in the report. The $U_{eq}$ for one of the Cr cation (0.117(4)) was twice that of the other two metal ions (Mn(1): 0.0135(9), Cr(1): 0.033(1), Mn(2): 0.063(1)) and larger than that of virtually all the light atoms, surely an unreasonable occurrence. Finally, we note that in the similar structure of RUPBEJ[123] where there is an identical $MnCr(Ox)_3$ with a different cation, for RUPBEJ the cation is tetra(*n*-propyl)ammonium where for PINFOH it is triphenylphosphonium, the BVS was determined as 2.80; in this case, a much better result. Consequently, one should view the PINFOH report with some skepticism. Deviant BVS sums are a good indicator of a poor structure determination and thus PINFOH was not used.

Cr(V) and Cr(VI) complexes. The situation with Cr(V) and Cr(VI) complexes is much more complicated. Here, the average $R_0$ did not have as much success in calculating a BVS that was close to the theoretical state. In the case of Cr(V) complexes retrieved from the CSD, they all appear to have CN = 5, while the Cr(VI) case has CN = 4. Therefore, in the case of Cr(V) and Cr(VI), we have examples of complexes with high oxidation states but low coordination numbers, presenting a special problem for BVS calculation. This class of compounds does not appear to be amenable to an oxidation state independent value since the O···O contacts are much shorter than Van der Waals contacts, thus any shortening of the Cr-O bonds to increase the BVS would be impossible. A somewhat similar conclusion had been reached using a different approach.[124] These conclusions are supported by the Cr-O bond length analysis carried out in conjunction with the structure determination of FURNIP.[125] In this analysis, the Cr-O mean bond lengths for monochromate ions were determined as 1.646(25) Å. With increasing polymerization, a change from monochromates to dichromates, the bridging Cr-O bonds increase while non-bridging terminal Cr-O bonds decrease in comparison with the monochromate Cr-O bonds. For dichromates the bridging bonds are 1.780(7) Å long while the non-bridging terminal bonds are 1.615(18) Å long. With further polymerization, when there is a change from dichromates to trichromates, the bridging bonds increase while the terminal bonds decrease again. The trend continues going from trichromates to tetrachromates and then from tetrachromates to polychromates. These changes are understandable in terms of maintaining the BVS around the various Cr atoms; a longer Cr-O bridge bond means less valence contribution, thus necessitating a decrease in the terminal bonds so overall BVS does not change. Consequently, the BVS for these complexes are smaller than expected if an average $R_0$ value is used. A further complication arises in the case of Cr(VI) complexes since a number of the chromates and dichromates are disordered. For example, the complexes ZAWWID,[126] ZAWWOJ,[127] and ZOKYUT[128] were retrieved as having CN=5 but in reality are disordered $CrO_4^{2-}$ ions: examination of the reports confirmed this. For this reason, we looked for an example of a Cr complex with a high oxidation state and a high coordination number. This led us to $K_3Cr(O_2)_4$, a Cr(V) with CN = 8 complex.

The structure of the $K_3Cr(O_2)_4$ complex was originally determined using film data and was not well refined.[111] Two subsequent papers refined the same data so that there were three different parameter sets and distances for this complex from only one data set. To resolve the differences and to provide a more accurate determination the complex was synthesized and the structure redetermined. The complex was synthesized using a slightly modified published procedure.[130] X-ray structure determination[131] was conducted by Dr. Khalil A. Abboud of the Department of Chemistry at the University of Florida. A view of the complex is given in Figure 4-1. The O-O distance of 1.452(2) Å is almost the average of the three previous determinations, two of which are longer[111,112] (1.489(22)[111] and 1.47(3) Å[112]) and the other[113] (1.405(39) Å) shorter. The O-O distance is very close to the O-O distance in various peroxides[129] that is in agreement with the formulation as a Cr(V) species. Our results are also in agreement with the proposed bonding in this complex.[108] The BVS using our average $R_0$ is 4.74, is in agreement with the expected value. This result suggests that our average value will provide a good estimate of the oxidation state except for those cases where a combination of high oxidation state and low coordination number exists in the complex. In these cases, the BVS will usually be low.

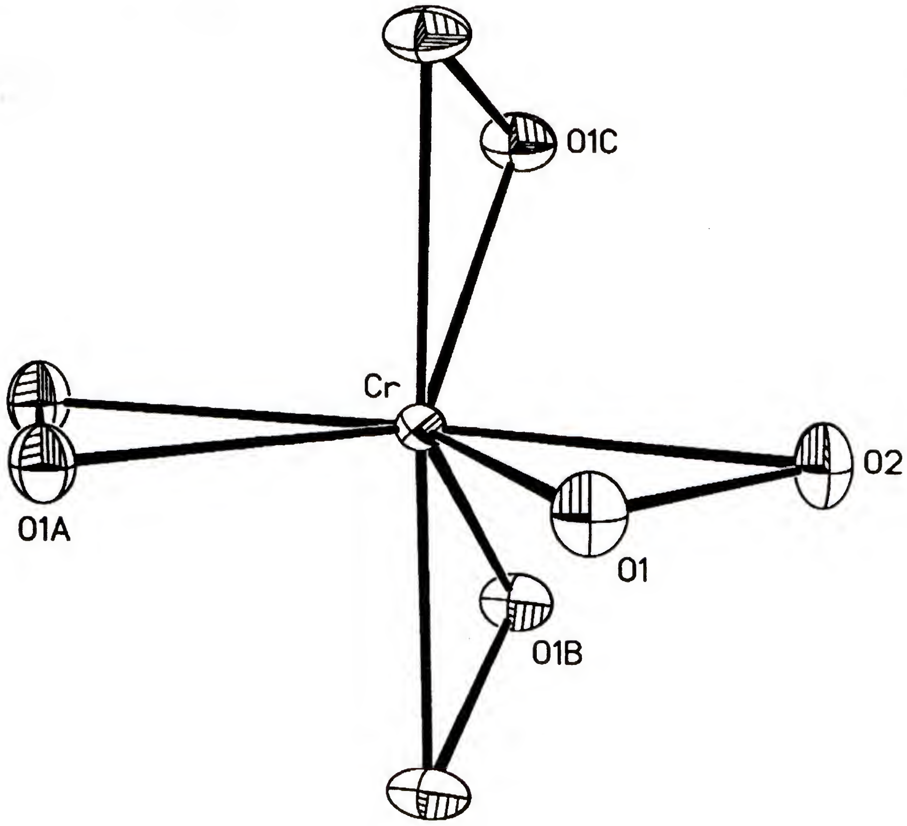

Figure 4-1. ORTEP drawing of $K_3Cr(O_2)_4$.

Distances in Cr complexes. The bond distance data for those complexes used in our analysis are summarized in Table 4-3. We see that for a given oxidation state and coordination number there is a wide range of Cr-O distances, but the average corresponds, in most cases, to a valence per bond equal to the oxidation number divided by the CN. We see that in the case of Cr(VI) with CN = 4, the average valence, calculated using Equation (13) is only 1.23, not the 1.5 that might be expected. This observation is in agreement with the fact that the O····O distance is very short and that repulsions between the O atoms prevent a shortening of the bond. The fact that these complexes are good oxidizing agents is explicable in terms of their lower BVS.

Conclusions for Cr-O complexes. The BVS is a relatively simple calculation if the appropriate $R_0$ values are available. For the Cr case with O donor atoms, we have shown that an $R_0$ of 1.724 Å can be used to calculate the oxidation state of the Cr atom with no prior assumptions. The results are in agreement for oxidation states of Cr(II), Cr(III), and Cr(V). The agreement with Cr(VI) was not very good which may be a reflection of steric constraints with high oxidation states and low coordination numbers.

The deviation of the BVS from an integer value usually indicates either problems with the structure, possible steric constraints, or excessive thermal motion. We have provided a number of examples to illustrate these points.

In cases where the ligand oxidation state is ambiguous, the BVS can be used as a guide for the oxidation state of the metal and therefore, by inference, the ligand. The BVS can be extremely useful to chemists in evaluating the results of a crystal structure analysis or in resolving conflicts regarding oxidation states. Structural chemists should be able to utilize the BVS to support the crystal structure analysis. The concept can be applied without assumptions regarding the oxidation state and can help avoid serious errors prior to publication.

# CHAPTER 5

# POTASSIUM AND SODIUM COMPLEXES WITH OXYGEN AND NITROGEN DONORS

The study of potassium and sodium complexes with oxygen and nitrogen donor atoms (henceforth K-O,N and Na-O,N respectively) was undertaken for several reasons. The reported values of $R_0$ were all derived from ionic-type solids, and the question was whether values derived from coordination type complexes would be identical. There are no complications from multiple oxidation and/or spin states; therefore, the K and Na complexes should provide a clear picture of the consequences of a non-integer BVS together with the effect, if any, of the coordination number on the BVS calculation. Finally, discussions of the distances and the coordination around a $K^+$ or $Na^+$ ion are frequently not given although the data can provide not only chemical information but can be an indicator of the accuracy of the determination. A majority of the complexes with nitrogen donor atoms include oxygen-atom donors as well, thus necessitating the use of an $R_0$ K-O or Na-O value. Since the $R_0$ values for K-O and Na-O interactions have been satisfactorily determined in Chapter 2, we can use those values to help accurately pinpoint the $R_0$ value for the K-N and Na-N lengths. The relatively modest amount of discussion of K-N and Na-N distances in potassium and sodium complexes may be due to the misconception that the bonding is strictly ionic and perhaps uninteresting, as well as the lack of a current compilation of K-N and Na-N distances to which reported structures can be compared. As follows, it shall be shown that a tabulation of the various M-N (M

= K or Na) distances as a function of coordination number can be used in a thoughtful discussion of M-N bond lengths. Hopefully, the new K-N and Na-N $R_0$ values determined will be used in routine calculations for K and Na compounds in all future crystal structure reports.

## Experimental Section

K-O,N and Na-O,N complexes. The bond length data for both K-O,N and Na-O,N sets was obtained from the April 1998 release of the Cambridge Structural Database containing 181309[22] entries. For a given coordination number, n, only those entries containing at least one N atom were retrieved, i.e. $MO_nN_m$ (M = K or Na, m=1-8, n=0-7). Using the $R_0$ values from Chapter 2, the $R_0$ for K-O was set at 2.113 Å while for Na-O the $R_0$ was set at 1.756 Å in Equation (13). Using those values an $R_0$ was then determined for K-N or Na-N interactions that minimized the difference between the assigned valence and the valence calculated for the BVS. Any entries that were deemed to be incorrect or very poor in crystallographic quality were removed (see Results and Discussion for individual cases). Then the $R_0$ was again determined for which the difference between assigned and calculated valence was minimized. The $R_0$ values determined in this way are given in Table 5-1 (K complexes) and 5-2 (Na complexes). A K-N $R_0$ of 2.105 Å and a Na-N $R_0$ of 1.935 Å were found with this method. In Tables 5-1 and 5-2 the $R_0$ values for each coordination number from three to eight are given for K-N and Na-N interactions respectively. As shown for both K and Na complexes, these values generally decrease as CN increases. For the sodium set, the value for CN=8 is higher than for CN=7, possibly due to increased steric crowding around the $Na^+$ ion.

The lists of the 238 $KO_nN_m$ and 242 $NaO_nN_m$ complexes ($n = 0\text{-}7$, $m = 1\text{-}8$), using the $R_0$ of 2.105 Å for K-N and 1.935 Å for Na-N, are included in the Appendices A and B, respectively. A tabulation of the K-N or Na-N bond length data as a function of coordination number is given in Tables 5-3 and 5-4, respectively. The BVS was calculated using a FORTRAN program written by Richard Wood (line coding for the program is provided in Appendix C).

Table 5-1. Summary of BVS calculations for various K complexes with O and N donors.

| CN | No | $R_0$ K-N |
|---|---|---|
| 4 | 3 | 2.360 |
| 5 | 8 | 2.284 |
| 6 | 18 | 2.186 |
| 7 | 24 | 1.988 |
| 8 | 184 | 1.906 |
| All | 237 | 2.105 |

Note: CN is the coordination number, No is the number of complexes used in determining that particular $R_0$ value, $R_0$ (in Å) is the value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states.

Table 5-2. Summary of BVS calculations for various Na complexes with O and N donors.

| CN | No | $R_0$ Na-N |
|---|---|---|
| 3 | 10 | 1.968 |
| 4 | 70 | 1.962 |
| 5 | 36 | 1.903 |
| 6 | 44 | 1.847 |
| 7 | 34 | 1.843 |
| 8 | 46 | 1.915 |
| All | 240 | 1.935 |

Note: CN is the coordination number, No is the number of complexes used in determining that particular $R_0$ value, $R_0$ (in Å) is the value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states.

Table 5-3. Summary of the distances (in Å) used in the K-O,N analysis.

| CN | Atom | No | Avg | Sigma | Min | Max |
|---|---|---|---|---|---|---|
| 4 | O | 7 | 2.670 | 0.050 | 2.565 | 2.705 |
| 5 | O | 27 | 2.734 | 0.093 | 2.526 | 2.904 |
| 6 | O | 49 | 2.799 | 0.108 | 2.616 | 3.377 |
| 7 | O | 126 | 2.792 | 0.088 | 2.596 | 3.081 |
| 8 | O | 1105 | 2.824 | 0.055 | 2.611 | 3.254 |
| 4 | N | 5 | 2.810 | 0.029 | 2.763 | 2.833 |
| 5 | N | 13 | 2.838 | 0.076 | 2.689 | 2.992 |
| 6 | N | 59 | 2.864 | 0.084 | 2.730 | 3.067 |
| 7 | N | 42 | 2.860 | 0.099 | 2.679 | 3.093 |
| 8 | N | 375 | 2.983 | 0.060 | 2.737 | 3.226 |

Note: CN is the coordination number, Atom is the atom type, No is the number of bonds used to compute the average bond length, Avg, and the calculated sigma, Sigma. Min is the minimum bond length found in the sample set and Max is the maximum bond length found in the set.

Table 5-4. Summary of the distances (in Å) used in the Na-O,N analysis.

| CN | Atom | No | Avg | Sigma | Min | Max |
|---|---|---|---|---|---|---|
| 3 | O | 5 | 2.281 | 0.034 | 2.239 | 2.328 |
| 4 | O | 70 | 2.327 | 0.079 | 2.199 | 2.598 |
| 5 | O | 88 | 2.501 | 0.081 | 2.192 | 2.624 |
| 6 | O | 178 | 2.445 | 0.097 | 2.048 | 2.877 |
| 7 | O | 183 | 2.488 | 0.109 | 2.258 | 2.917 |
| 8 | O | 244 | 2.752 | 0.079 | 2.312 | 2.788 |
| 3 | N | 25 | 2.394 | 0.083 | 2.275 | 2.595 |
| 4 | N | 210 | 2.495 | 0.161 | 2.242 | 3.231 |
| 5 | N | 92 | 2.501 | 0.086 | 2.354 | 2.837 |
| 6 | N | 86 | 2.521 | 0.137 | 2.303 | 2.926 |
| 7 | N | 55 | 2.593 | 0.127 | 2.334 | 2.995 |
| 8 | N | 124 | 2.752 | 0.147 | 2.456 | 3.435 |

Note: CN is the coordination number, Atom is the atom type, No is the number of bonds used to compute the average bond length, Avg, and the calculated sigma, Sigma. Min is the minimum bond length found in the sample set and Max is the maximum bond length found in the set.

## Results and Discussion

### K-O,N Complexes

The K-N $R_0$ of 2.105 Å is slightly different from the ionic compound value of 2.26 Å[27] and the empirical value of 2.29 Å[28]. The difference is not surprising due to the relatively small number of potassium-nitrogen compounds (as opposed to potassium-oxygen structures, for example). There were five complexes whose BVS was greater or less than 0.3 from the expected value and a sigma of 0.118. In comparison, the value 2.275 Å (chosen since it was about the average of the two literature values) was used to see how the literature values stacked up. The sigma was 0.206 for the $R_0$ of 2.275Å. There were 24 complexes whose BVS were greater or less than 1.0 by 0.3--thus showing our value of 2.105 Å as a significant improvement.

The majority of three- and four-coordinate potassium complexes with only K-N and K-O interactions had BVS values that were much lower than 1. When the reports of those complexes were examined, a great number of these revealed K-C interactions not included in the CSD file. Of the CN=3 complexes, GINMEV[132] (BVS = 0.52, 0.51, 0.51, 0.50), HIXGOK[133] (0.41), PONYOG[134] (0.56), and REMGEV[135] (0.48) all were confirmed to have K-C interactions. Of the CN=4 complexes, GINMEV[132,*](0.48, 0.46), JOQFIE[136] (0.57), KIYZIB[137] (0.43), NIMSEH[138] (0.81), PONYOG[134,#] (0.79), REMGEV[135,#] (0.65), VOHXUL[139] (0.63), and ZEDVIN[140] (BVS = 0.50, 0.50, 0.51) also

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[*] GINMEV has two crystallographically different K ions where the CNs are different.

[#] Both PONYOG and REMGEV are potassium potassiates, characterised with two distinct types of K centers. For these complexes the different K centers have different CNs.

had K-C interactions. The five-coordinate complex WECXIL[141] (0.58) and the six-coordinate NITFAX[142] (0.61) also had K-C interactions. In Chapter 2, the study of KO complexes showed that lower coordination complexes can add extra interactions with carbon atoms and thus raise the BVS to a value closer to the expected. As with the examples given in Chapter 2, the complex NIMSEH was characterized by an interaction of potassium with an anionic carbon ring in Table 5-5; the BVS was calculated for both coordination numbers six and seven. For the majority of the previously listed complexes, however, the K-C contributions to valence appear marginal. All of the previously listed complexes, whether the K-C valence contribution was significant or not, were not used in the analysis to determine the K-N $R_0$ due to the K-C interactions.

There is a strong suspicion that the CN=3 complex SAMMEY[143] (BVS = 0.50) has K-C interactions. While the figure of the structure[143] does not show actual potassium-carbon interactions, the figure does list two K-C lengths of 3.38(1) and 3.42(1) Å. The valence contributions for these two interactions totals 0.14, redetermining the BVS as 0.64 and illustrating an increase closer to 1. Considering the dearth of three-coordinate potassium-oxygen complexes, as shown in Chapter 2, it is probable that SAMMEY's CN is actually higher. This structure therefore was not used.

The report for CN=4 complex JECFEC[144] (BVS = 0.59) revealed in addition to the four ligating CN groups coordinated to the K ion there were also four pyridine bridging groups coordinated to the K ion as well. Using the PARST program, the four extra K-N lengths were calculated as 3.02 Å. The BVS was redetermined at 0.92 with the additional valence of the four extra K-N interactions. This type of coordination number designation error, while rare in the CSD, occurs occasionally.

Table 5-5. K-O,N complexes with K-$C_{(ring)}$ interactions.

| REFCODE | n | K-O,N val | K-$C_{avg}$ | K-C val | BVS-6 | BVS-7 |
|---|---|---|---|---|---|---|
| NIMSEH[138] | 4 | 0.79 | 3.43 | 0.065 | 0.92 | 0.98 |
| NIMSEH[138] | 4 | 0.81 | 3.16 | 0.135 | 1.08 | 1.21 |

Note: REFCODE is the code used in the CSD file, n is the number of O and N atoms coordinated to K, K-O,N val is the valence sum for the oxygen and nitrogen donors, K-$C_{avg}$ is the average K-C distance (in Å) , K-C val is the valence of the K-$C_{avg}$ distances using $R_0$ = 2.419 Å for the K-C bond, BVS-6 is the BVS assuming a coordination number of 6 for K achieved by forming 6-n K-C bonds, and BVS-7 is the BVS assuming a coordination number of 7 for K achieved by forming 7-n K-C bonds.

Another CN=4 complex, RAFSUM[145] (BVS = 0.60), is actually ten-coordinate; inspection of the figure 1[145] shows six K-H interactions. The PARST program calculated the K-H distances at 2.77, 3.28, 3.51, 3.85, 3.63, 2.95, and 3.98 Å. Using the valence program ($R_0$ for K-H = 2.11 Å), the BVS was redetermined as 0.96. The authors state that they believe the H-K interactions are more likely to be electrostatic than covalent. The use of the BVS, however, indicates a significant degree of covalency.

The structure WEBHIU[146] was found in the CSD file as both three- (BVS = 0.16) and seven-coordinate (BVS = 0.44) forms. Examination of the report revealed that the actual coordination was seven. The structure is a polymeric one which probably explains the CN=3 listing. While the K-N lengths are unusually long--there are three K-N lengths 3.368 Å long or greater--there is a lack of information about this structure that hampered our ability to evaluate it. Therefore it was discarded.

For SARHUO[147] (BVS = 0.66) and GAQTOH[148] (BVS = 0.55, 0.58), steric hindrance of the ligands probably contribute to the low BVS. For SARHUO sterically bulky trimethylsilyl, tertiary-butyl (t-butyl), and bipyridine (bipy) groups play a role in keeping the donor oxygen and nitrogen atoms from approaching too closely. For GAQTOH, potassium ions are coordinated to N,N,N',N'-tetramethylethylenediamine (TMEDA) ligands which have a limited bite size. Thus, in order to avoid too much strain in the TMEDA ligand the K-N lengths will increase. For these reasons we discontinued using SARHUO and GAQTOH.

VOVGIW[149] and VOVGUI[150] (BVS = 0.70 each) both feature a mixed-alkali structure--VOVGIW has both Li and K while VOVGUI has Na and K--where the more electropositive alkali atom slightly draws the bridging nitrogen atoms of the two hexamethyldisilazanide (HMDS) bases toward it, away from the $K^+$ ion. For VOVGIW the Li-N bonds were 2.053(5) Å while the K-N bonds were 2.832(3) Å. For VOVGUI the Na-N bonds were 2.365(3) Å while the K-N bonds were 2.810(3) Å. In comparison to a similar symmetric dimer HMDS structure that contains only potassium cations, the K-N bonds were of the lengths 2.745(3) and 2.801(3) Å;[151] thus the K-N lengths in VOVGIW and VOVGUI are slightly longer. Since the BVS for VOVGIW and VOVGUI were not extremely low they were retained for the analysis but the reason for their slightly lower values is known.

YAKKOK,[152] BVS = 1.68, is a polymeric complex featuring both K and Cr(III) ions in the structure. The potassium ion is coordinated with six N atoms to give a $KN_6$ octahedron with two bridging azide ions to the chromium. The K-N bond lengths are reported at 2.556(5), 2.572(5), and 2.603(5) Å--shorter than other reported $KN_6$

octahedra.[153-155] Besides potassium, sodium and rubidium analogues were prepared. The Rb-N lengths are longer than the K-N interactions as expected, but the Na-N lengths[156] are very close to the K-N ones, differing by only a few hundredths of an angstrom. Using the valence program we find that if sodium was substituted for potassium the BVS would drop much closer to 1. While we are unsure about the nature of the potassium ion, the high BVS led us to discard this complex.

CICDEX[157], BVS =1.46, an eight-coordinate complex, raises questions regarding the crystallographic quality. This complex has several short K-O and K-N bonds with one K-O being unusually short at 2.58(1) Å. Poor crystal quality makes it very difficult to evaluate the structure. Only 1465 reflections were observed out of a total of 3537. Plus, the authors describe the crystal quality as “miserable” (157, p.185). Thus, CICDEX was discarded.

COYDEZ[158], an eight-coordinate structure, has a grossly high BVS of 2.11. Examination of the reports shows there is disorder of the K(2,2,2-Crypt) cation. A lack of bond length and atomic coordinate information for this cation prevents us from discerning more closely the magnitude of this disorder. The synthesis section of the report did not indicate any use of sodium compounds for the making of the potassium cryptand. But the K-O and K-N values are generally in the range more suitable for sodium. Using the valence program the BVS was calculated to be about 0.85. We cannot say for certain though whether sodium is involved but since the actual BVS is very much different from expected we declined to use this structure in our final analysis.

For POPVEV[159], CN=6 and BVS=2.07, the question of the potassium-donor atom lengths leads us to ask whether the potassium ion is actually gold(I). The short K-N bond lengths--attributed by the authors as very strong binding of the potassium ion by the nitrogens of the 2,7-bis(diphenylphosphino)-1,8-naphthyridine ligands--fit within reason for Au-N interactions since the ionic radius for $Au^+$ is similar to $K^+$. Because atomic coordinate and isotropic displacement factor data were not included we cannot further evaluate that possibility. Also, there is a paucity of Au-N complexes for comparison. A BVS of about 1.15 was determined using the valence program. POPVEV was not used.

ZUGBOS[160] is listed in the CSD as a four-coordinate complex but examination of its report reveals a coordination of six. There are other questions with this structure. The BVS is very high at 1.82. Examination of K-N and K-O bond lengths show very short distances for the majority of the bonds. The bond lengths (the K-O lengths are 2.34(1), 2.34(1), 2.48(3), and 2.72(3) Å while the two K-N distances are 2.47(2) and 2.50(2) Å) are more appropriate for Na-N and Na-O bonds. Indeed, using the valence program the BVS drops to about 1.02. Examination of the experimental procedure does not show any potassium compound used in the synthesis. Thus, we cannot say with hard certainty the exact nature of the cation. Because of the uncertainty we did not use this structure in the analysis.

Conclusions for K-O,N complexes. We have shown that for 237 $KO_nN_m$ complexes that a $R_0$ of 2.105 Å used in Equation (13) gives a BVS of 1 in most cases. When the BVS differs markedly from 1, there are usually problems with the crystal structure, misidentified cations, and unnoticed or unreported interactions. Therefore, one use of the BVS is confirmation of the crystal structure determination. However, equally or even more important is the insight into chemical bonding provided by this simple calculation. Complexes that were reported with a coordination number of three in reality had higher CNs with the missing interactions in the form of potassium-carbon bonds. Potassium complexes with three-coordination are rarely seen; the BVS is often low due to steric reasons and higher BVS values can be obtained via reactions where the end product has a higher coordination. The $R_0$ of 2.105 Å is influenced by the great number of eight-coordination structures found relative to CN=4-8. Yet, the value worked well for all coordination numbers used in this study. In summary, the BVS is a simple calculation that can be used to understand the bonding in these complexes as well as to avoid introducing errors into the literature.

Na-O,N Complexes

The Na-N $R_0$ of 1.935 Å is similar to the ionic compound value of 1.93 Å[28] and the empirical value of 1.968 Å.[26] When the $R_0$ of 1.935 Å was used, the results included a sigma of 0.139 and only four complexes having a BVS that was greater or less than 0.3 from 1.0. In comparison, for the ionic value 1.968 Å--used to see how the literature values compared--there was a sigma of 0.153 and 14 complexes whose BVS were greater or less than 1.0 by 0.3.

Many three-coordinate structures taken from the CSD had extra interactions that were not included in the CN.[12-14] Examples of this are included in Chapters 2 and 3. For the sodium-oxygen/nitrogen environment, there are several examples of low CN complexes with extra interactions. The complexes of JUNRIT[161] (BVS = 0.61, 0.68), RILMII[162] (0.73), SEBJUE[163] (0.54, 0.52), and YUPKAV[164] (0.60) were listed as three-coordinate in the CSD. Examination of the reports showed that the Na ions were coordinated to saturated carbons, in Table 5-7, which were not factored in the coordination for the CSD. The valences of the Na-C interactions were calculated by using the valence computer program. It is postulated that the additional interactions raise the

BVS closer to 1.0. Factoring all the Na-C interactions, however, would grossly increase the BVS for JUNRIT, SEBJUE, and YUPKAV. Even though the a new, redetermined BVS cannot be calculated, these complexes were not used due to the K-C interactions; the exact CN of the central Na cannot be pinpointed as with the anionic organic ring examples of Chapter 2. For RILMII, the PARST program was used to determine one Na-C interaction of 2.963 Å, contributing 0.23 in valence. The BVS was redetermined as 0.96. It should be noted for RILMII that the crystallographic quality is suspect: the *R* factor value is very high at 0.169 and only 3129 out of 6769 reflections are used.

The complexes REGTEC[165] (BVS = 0.70) and DETPIB[166] (BVS = 0.75) were both entered in the CSD with incorrect CNs. While errors are relatively rare in the CSD, especially considering the large number of entries, they do occur. The CNs found in the CSD file were smaller than actual. REGTEC, original BVS = 0.70 and original CN=4, was a polymeric compound where an extra bond linking adjacent chains of sodium pyruvic acid oxime (NaPAO) units raises the CN. Plus, an interaction of extra water molecules to sodium was not included in the CSD file. The extra interactions--two normal lengths of 2.588(2), 2.530(2) and one long length 2.917(2)--raise the BVS to a more acceptable value of about 0.97. For DETPIB, a tris(phenanthroline) macrobicyclic ligand encapsulates a sodium ion with the six nitrogen atoms of the three phenanthroline ligands coordinated to the sodium. The bridgehead nitrogens of the ligand are also coordinated to the sodium--in the CSD file those two interactions were not included--at lengths of 2.774(10) and 2.805(10) Å to give an eight-coordination sodium complex. The new BVS was redetermined as 0.90. These two complexes were relisted by their new coordination numbers in our set.

Table 5-7. Na-O,N complexes with Na-C interactions.

| REFCODE | n | Na-O,N val | Na-C | Na-C val |
|---|---|---|---|---|
| JUNRIT[161] | 3 | 0.61 | 2.791 | 0.366 |
| | | | 2.654 | 0.530 |
| | | | 2.797 | 0.360 |
| JUNRIT[161] | 3 | 0.68 | 2.832 | 0.328 |
| | | | 2.707 | 0.459 |
| | | | 2.724 | 0.439 |
| RILMII[162] | 3 | 0.73 | 2.963 | 0.230 |
| SEBJUE[163] | 3 | 0.54 | 2.891 | 0.279 |
| | | | 2.730 | 0.432 |
| SEBJUE[163] | 3 | 0.52 | 2.789 | 0.368 |
| | | | 2.748 | 0.410 |
| YUPKAV[164] | 3 | 0.60 | 2.702 | 0.465 |
| | | | 2.716 | 0.448 |

Note: REFCODE is the code used in the CSD file, n is the number of O and N atoms coordinated to Na, Na-O,N val is the valence sum for the oxygen and nitrogen donors, Na-C is the distance of the respective Na-C interaction (in Å) , Na-C val is the valence of the Na-C distances using $R_0 = 2.419$ Å for the Na-C bond.

For DUSVAO10,[167] BVS = 2.21, there is a three-dimensional framework of a cristobalite type structure where Na and Hg(II) ions are linked via cyano groups in the form of linear Na-N≡C-Hg bridges. Tetraethylammonium, $NEt_4^+$, cations sit in cavities in the structure. The main question is whether the alleged sodium cation is really sodium or in fact actually mercury. The listed Na-N distances of 2.154(39) Å are very similar to the Hg-C lengths of 2.214(35) Å and the BVS of 2.21 is reasonable for a Hg(II) ion. Thermal parameters were not included in the report so we could not determine with absolute certainty the nature of the cation. Therefore, it was decided to not use DUSVAO10.

For KOCNAR[168] (BVS = 1.31, 1.37, 1.41), KOCMUK[169] (1.23, 1.34, 1.44), and SUMFOV[170] (1.34) there are questions about the crystallographic quality. The BVS values for these complexes were much higher than the majority of the other five- and six-coordinate complexes. The crystal sizes for these are reasonable (KOCMUK 0.20 x 0.28 x 0.30 mm, KOCNAR 0.25 x 0.30 x 0.36, for SUMFOV the crystal size was not included). However, the number of observed data are less than half of the total data, usually an indicator of possible problems with crystal quality and thus the bond data. For KOCMUK only 2118 out of 7270 reflections were used while for KOCNAR 5054 out of 11279 were used. For SUMFOV 1302 out of 4834 were used. For this reason these three complexes were discarded.

Questions about the crystallographic quality were present with CRNASN01[171] (BVS = 0.70, 0.90, 0.90, 0.82--formula $(C_{18}H_{36}N_2O_6 \bullet Na^+)_3Sb_7^{3-}$) and CRSHSB10[172] (BVS = 0.87, 0.73, 0.53--formula $(\text{crypt-}Na^+)_4Sn_9^{4-}$). The sodium cation associated with the lowest BVS value of CRNASN01, 0.70, had a very high temperature factor parameter

($\beta_{33}$ was 14.8(16)). This value is much higher when compared to the other sodium and tin atoms of that complex. The $\beta_{33}$ values for other Na and Sn atoms ranged from 5.0 to 6.9. A similar situation exists for CRSHSB10 where the $\beta_{22}$ values for the sodium atoms with the two lowest-BVS values (0.73 and 0.53) are 12(1) and 13(1). Those values are twice as high as for the $\beta_{22}$ value (6.8(8)) of the sodium atom with the reasonable BVS of 0.87. Additional difficulties arise with CRNASN01 where the crypt-$Na^+$(1)--the sodium with the high $\beta_{33}$--is described as a six-coordinate structure. The authors report that strain is responsible for "the first reported example of a reduction in the coordination number of 2,2,2-crypt from 8 to 6" (171, p. 3315). We find that this situation is questionable since the authors state that "the packing considerations necessary to capture this particular configuration in the present compound must be very subtle" (171, p.3316,3317). For CRSHSB10, there was difficulty in locating and refining the sets of atoms making up two crypt molecules. Also, for crypt two (BVS=0.73) there were very large thermal parameters for the bridgehead ethylene groups while for crypt three there was disordering of those groups. Because of this and because of the very high *R* factor values--for CRNASN01 it was 0.121 and for CRSHSB10, 0.111--these two complexes were not used due to serious questions about the quality of the data.

Conclusions for Na-O,N complexes. We have shown that for 241 $NaO_nN_m$ complexes where a $R_0$ of 1.935 Å used in Equation (13) gives a BVS of 1 in most cases. When the BVS differs markedly from 1, there are usually problems with the crystal structure, misidentified cations, and unnoticed or unreported interactions. Therefore, one use of the BVS is confirmation of the crystal structure determination. However, equally or even more important is the insight into chemical bonding provided by this simple calculation. Complexes that were reported with a coordination number of three in reality had higher CNs with the missing interactions in the form of sodium-carbon bonds. Sodium complexes with three-coordination are relatively rare compared with the higher coordination numbers; the BVS is often low due to steric reasons and higher BVS values can be obtained via reactions where the end product has a higher coordination. The $R_0$ of 1.935 Å works very well for the majority of structures with CN=4-8. There are no major differences between complexes that have only nitrogen-atom donors and those with both nitrogen- and oxygen-atom donors. In summary, the BVS is a simple calculation that can be used to understand the bonding in these complexes as well as to avoid introducing errors into the literature.

# CHAPTER 6
# NICKEL (II) 2-ACETYLPYRIDINE THIOSEMICARBAZONES

Various transition metal complexes of 2-acetylpyridine thiosemicarbazones have been tested against several types of pathogens for evidence of biocidal activity.[173] Included in this group, nickel (II) $N^4$-substituted 2-acetylpyridine thiosemicarbazones have been synthesized and tested for activity.[18,173] The focus of this dissertation is on nickel (II) [$N^4$-unsubstituted] 2-acetylpyridine thiosemicarbazone complexes. Attempts were made to synthesize the structures of both nickel (II) mono- and di-substituted 2-acetylpyridine thiosemicarbazone. The synthesized complex was then tested for biocidal activity against various disease-causing agents.

## Ni (II) di-(2-acetylpyridine thiosemicarbazone)

Materials. Thiosemicarbazide, 2-acetylpyridine thiosemicarbazone, and nickel dinitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were all commercial products and used without further purification.

Synthesis. 2-acetylpyridine thiosemicarbazone was prepared by refluxing a 1:1 molar ratio of 2-acetylpyridine and thiosemicarbazide in 100% ethanol. Upon the reduction of volume the compound was isolated as a yellow solid (m.p. = 158-160). Anal. Calc(found) for $C_8H_{11}N_4S$: C, 49.50(49.01); H 5.19(5.77); N 28.85(26.84). Synthesis of Ni (II) di-(2-acetylpyridine thiosemicarbazone) was carried out by refluxing

0.103g (0.530 mmol) of 2-acetylpyridine thiosemicarbazone with 0.771g (0.265 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$ in 70 mL of $H_2O$. Anal. Calc (found) for $C_{16}H_{20}N_8SNi$: C, 31.65(32.30); H 3.98(3.77); N 23.07(23.09). Crystals suitable for an X-ray diffraction study were obtained after cooling the filtrate slowly over a period of weeks. Crystals were obtained as brown plates (dec. > 250).

X-ray determination. The intensity data were collected using a 0.24 x 0.22 x 0.19 mm crystal at 143 K on a Siemens Smart Platform equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using 32553 reflections. The relevant crystallographic data for Ni (II) di-(2-acetylpyridine thiosemicarbazone) dinitrate at 143 K: Empirical Formula = $C_{16}H_{24}N_{10}NiO_8S_2$, Formula weight = 607.28, Monoclinic, Space group P2(1)/n, a = 16.94300(10) Å, b = 13.7203(3) Å, c = 23.5334(3) Å, Vol = 5151.06(10) Å$^3$, Z = 8. Integration was used for absorption corrections. The structure was solved by direct methods and refinement by anisotropic least-squares on $F^2$ was carried out using SHELXTL5.[174] The final *R* values for all 11771 independent reflections were $R_1$ = 2.81% and w$R_2$ = 6.86%.

Discussion. A thermal ellipsoid drawing of the complex, given in Figure 6-1, shows the full nickel coordination sphere and the atomic numbering scheme including the 2-acetylpyridine thiosemicarbazone ligands and the two nitrate counteranions. Crystallographic data are given in Appendix Table D-1. Bond and angles are given in Appendix Table D-2. Atomic coordinates are given in Appendix Table D-3. Anisotropic displacement parameters are given in Appendix Table D-4. Hydrogen coordinates are given in Appendix Table D-5.

Each 2-acetylpyridine thiosemicarbazone ligand coordinates in a tridentate fashion through N1, N2, N11, N12, and the two thiocarbonyl sulfurs S1 and S11 to bring the total coordination number to six. The two nitrate counteranions maintain the charge balance. The two thiosemicarbazone ligands, in order to minimize steric interactions, are aligned close to right angles with one another, characterized with the S1-Ni1-S11 angle of 93.66°, N1-Ni1-N11 93.03°, N1-Ni1-S11 89.34°, and S1-Ni1-N11 90.43° (Table D-2).

Biocidal activity. The di-substituted complex was tested for signs of biocidal activity against several disease-causing agents. The complex was dissolved in EtOH. 0.1 mL samples of the dissolved compound were then added to 1 cm x 1 cm squares of filter paper. The squares were then added to plates that have been spread with various cultures of bacteria or yeasts and incubated at 35°C for 24 hours. No inhibition was observed with *escherichia coli* (gram negative bacterium), *staphylococcus aureus* (gram positive bacterium), *pseudomonas aeruginosa* (gram negative bacterium), and *candidad albicans* (yeast). The testing was conducted by Dr. Samuel Farrah of the Department of Microbiology and Cell Science.

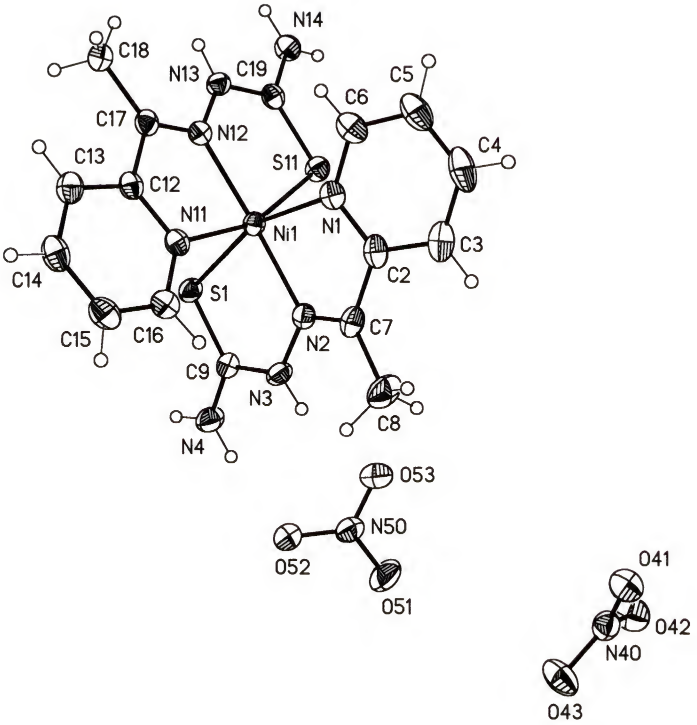

Figure 6-1. ORTEP drawing for Ni (II) di-(2-acetylpyrdine thiosemicarbazone) dinitrate

## Ni (II) mono-(2-Acetylpyridine thiosemicarbazone)

Synthesis attempts of Ni (II) mono-(2-acetylpyridine thiosemicarbazone). Several attempts were made to synthesize a Ni (II) mono-substituted 2-acetylpyridine thiosemicarbazone complex. A 1:1 molar quantity ratio of ligand and $NiCl_2 \cdot 6H_2O$ was refluxed; the resulting product was the di-substituted complex.

A recent report[175] put forth the claim of a synthesis of a Ni (II) mono-substituted 2-acetylpyridine thiosemicarbazone complex, arising from the reaction of $NiCl_2$ and the ligand in a 1:1 molar ratio. However, there are several points of contention that cast doubt. No X-ray analysis was performed. The authors' suggested structure[175] (Figure 6-2) was square planar where the nickel cation was coordinated to two $Cl^-$ anions and the pyridine and hydrazinic nitrogen atoms of the thiosemicarbazone ligand. The sulfur atom was shown not coordinated to the nickel. In the great majority of thiosemicarbazone complexes the sulfur atom is coordinated to the metal cation. Hence, the authors' suggested structure is extremely unusual in that respect. In addition, the color of a majority of nickel thiosemicarbazone complexes is usually reddish-brown to brown. The color of the authors' monosubstituted complex is green. Finally, the ligand in the complex is depicted as non-anionic; often the thiosemicarbazone ligand will lose a proton. It should also be noted that the authors' suggested structure for a Ni (II) di-substituted 2-acetylpyridine thiosemicarbazone complex was given as a CN=4 structure where the ligands' sulfur atoms were shown not coordinated to the nickel ion. In contrast, this dissertation shows the opposite for the sulfur atoms. Thus, the report given by the authors should be regarded at with some uncertainty.

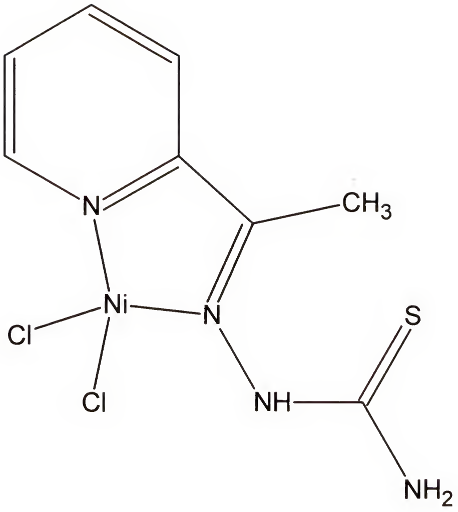

Figure 6-2. Suggested structure for Ni (II) mono-(2-acetylpyridine thiosemicarbazone) from reference 175.

# APPENDIX A
# LIST OF K-O,N COMPLEXES USED FOR THE BVS ANALYSIS

Appendix Table A-1. A listing of the BVS for the 238 $KO_nN_m$ (n = 0-6, m = 1-7) complexes used in the determination of K-N $R_0$ of 2.105 Å.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| **Coordination Number 4** | | | | | | |
| REMGOF | 0.046 | 1.00 | 0.88 | -0.121 | | N O O O |
| VOVGIW | 0.052 | 1.00 | 0.70 | -0.299 | | N N O O |
| VOVGUI | 0.046 | 1.00 | 0.70 | -0.299 | | N N O O |
| **Coordination Number 5** | | | | | | |
| PAZXET | 0.104 | 1.00 | 0.78 | -0.223 | | N N N N O |
| POQNUE | 0.056 | 1.00 | 1.14 | 0.138 | | N O O O O |
| SAVLEG | 0.099 | 1.00 | 0.96 | -0.040 | | N O O O O |
| ZALVOX | 0.056 | 1.00 | 0.87 | -0.131 | | N O O O O |
| ZALVOX | 0.056 | 1.00 | 0.87 | -0.133 | | N O O O O |
| ZALVUD | 0.041 | 1.00 | 0.83 | -0.165 | | N O O O O |
| ZALVUD | 0.041 | 1.00 | 0.82 | -0.179 | | N O O O O |
| ZOTKAU | 0.050 | 1.00 | 0.76 | -0.241 | | N N N O O |
| **Coordination Number 6** | | | | | | |
| HEDJEF | 0.044 | 1.00 | 0.90 | -0.101 | | N N O O O O |
| HEZMII | 0.056 | 1.00 | 0.97 | -0.033 | | N O O O O O |
| KEMRAV | 0.048 | 1.00 | 0.90 | -0.098 | | N O O O O N |
| KOXDZO | 0.065 | 1.00 | 0.84 | -0.161 | | N O O O O N |
| LIMRAA | 0.033 | 1.00 | 0.86 | -0.139 | | N O N O O O |
| NAFVEV | 0.045 | 1.00 | 0.58 | -0.421 | ****** | N N N N N N |
| NEBKIO | 0.045 | 1.00 | 0.75 | -0.246 | | N N N N N O |
| NEBKOU | 0.045 | 1.00 | 0.78 | -0.224 | | N N N N O O |
| NOMPEK | 0.048 | 1.00 | 0.75 | -0.245 | | N N N N O O |
| OAZKCN | 0.036 | 1.00 | 0.96 | -0.040 | | N O O O O O |
| PEJRUR | 0.107 | 1.00 | 1.04 | 0.043 | | N N O O O O |

Appendix Table A-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| RIBMAQ01 | 0.088 | 1.00 | 0.81 | -0.189 | N N N N N N |
| RIBMAQ01 | 0.088 | 1.00 | 0.86 | -0.142 | N N N N N N |
| SAJMUL | 0.052 | 1.00 | 0.88 | -0.120 | N O O O O O |
| VOGREO | 0.056 | 1.00 | 1.02 | 0.021 | N N O O O O |
| VOVTIJ | 0.074 | 1.00 | 0.99 | -0.012 | N N N N N N |
| WAPTEM | 0.039 | 1.00 | 0.94 | -0.059 | N N O N N N |
| YAHLAU | 0.082 | 1.00 | 0.87 | -0.130 | N N O O O O |

**Coordination Number 7**

| | | | | | |
|---|---|---|---|---|---|
| COVPEI | 0.083 | 1.00 | 0.99 | -0.008 | N O O O O O O |
| COWSAI | 0.046 | 1.00 | 0.96 | -0.043 | N O O O O N O |
| COWSEM | 0.034 | 1.00 | 0.95 | -0.049 | N O O O O O N |
| DKCRKT10 | 0.016 | 1.00 | 1.16 | 0.163 | N O O O O O O |
| DUGBOW01 | 0.075 | 1.00 | 1.01 | 0.011 | N N O O O O O |
| DUJROP | 0.116 | 1.00 | 1.26 | 0.259 | N O O O O O O |
| DUJROP | 0.116 | 1.00 | 1.23 | 0.228 | N O O O O O O |
| FEXTEH | 0.065 | 1.00 | 1.15 | 0.146 | N O O O O O O |
| FUCLUK | 0.075 | 1.00 | 1.09 | 0.091 | N O O O O O N |
| FUCPEY | 0.048 | 1.00 | 1.27 | 0.272 | N O O O O O O |
| GACDAP | 0.074 | 1.00 | 1.04 | 0.043 | N O O N O O O |
| GIFJUA | 0.043 | 1.00 | 1.15 | 0.153 | N O O O O O O |
| GOCTEX | 0.032 | 1.00 | 1.06 | 0.063 | N O O O O O O |
| HBXCTK | 0.079 | 1.00 | 0.97 | -0.030 | N O O N O O O |
| HILTEB | 0.038 | 1.00 | 0.96 | -0.036 | N N N N O O O |
| NILQOO | 0.031 | 1.00 | 1.21 | 0.212 | N O O O O O O |
| NUDROT | 0.031 | 1.00 | 1.05 | 0.053 | N O O O O O N |
| PATDOD | 0.037 | 1.00 | 1.06 | 0.064 | N O O N O O O |
| PATDUJ | 0.049 | 1.00 | 0.96 | -0.036 | N O O N O O N |
| SEKTOR10 | 0.104 | 1.00 | 1.08 | 0.085 | N N O O O O N |
| SEKTOR10 | 0.104 | 1.00 | 1.19 | 0.186 | N N O O O O N |
| TOZPIH | 0.051 | 1.00 | 1.13 | 0.132 | N O O O O N O |
| VUYZEU | 0.042 | 1.00 | 1.22 | 0.220 | N O O O O O O |
| WIPSIX | 0.050 | 1.00 | 1.13 | 0.128 | N O O O O O O |

**Coordination Number 8**

| | | | | | |
|---|---|---|---|---|---|
| BAKYIV | 0.097 | 1.00 | 1.02 | 0.021 | O N N O O O O O |
| BAKYIV | 0.097 | 1.00 | 1.09 | 0.088 | O N N O O O O O |
| BEGJOM | 0.049 | 1.00 | 1.08 | 0.079 | O N N O O O O O |
| BIBMOO | 0.046 | 1.00 | 1.03 | 0.027 | O N N O O O O O |

Appendix Table A-1 continued.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| BIFWOC | 0.082 | 1.00 | 1.01 | 0.010 | | O N N O O O O O |
| BIFWOC | 0.082 | 1.00 | 1.06 | 0.063 | | O N N O O O O O |
| BIFWOC | 0.082 | 1.00 | 1.03 | 0.034 | | O N N O O O O O |
| BIGFOM | 0.084 | 1.00 | 1.17 | 0.166 | | O N N O O O O O |
| BIVNID10 | 0.065 | 1.00 | 1.17 | 0.166 | | O N N N N O O O |
| BIVNID10 | 0.065 | 1.00 | 1.14 | 0.140 | | O N N N N O O O |
| CASLUD | 0.053 | 1.00 | 0.98 | -0.017 | | O N O O O O O O |
| CIFJEG | 0.075 | 1.00 | 1.02 | 0.020 | | O N N O O O O O |
| CIFJEG | 0.075 | 1.00 | 1.06 | 0.055 | | O N N O O O O O |
| CIFJEG | 0.075 | 1.00 | 1.06 | 0.061 | | O N N O O O O O |
| CRPKTE | 0.094 | 1.00 | 1.08 | 0.076 | | O N N O O O O O |
| CRPKTE | 0.094 | 1.00 | 1.05 | 0.054 | | O N N O O O O O |
| CRYGER | 0.149 | 1.00 | 1.10 | 0.098 | | O N N O O O O O |
| CRYGER | 0.149 | 1.00 | 1.04 | 0.038 | | O N N O O O O O |
| CUPPEI | 0.068 | 1.00 | 1.03 | 0.029 | | O N N O O O O O |
| CUPPEI | 0.068 | 1.00 | 1.12 | 0.119 | | O N N O O O O O |
| DUGHIW | 0.027 | 1.00 | 1.06 | 0.058 | | O N N O O O O O |
| DUGJAQ | 0.029 | 1.00 | 1.07 | 0.072 | | O N N O O O O O |
| FAGSIP | 0.055 | 1.00 | 1.01 | 0.005 | | O N O O O O O O |
| FIHCOO | 0.082 | 1.00 | 1.10 | 0.102 | | O N N O O O O O |
| FIHCOO | 0.082 | 1.00 | 1.10 | 0.096 | | O N N O O O O O |
| FIHCUU | 0.083 | 1.00 | 1.20 | 0.197 | | O N N O O O O O |
| FISGUJ10 | 0.035 | 1.00 | 1.16 | 0.164 | | O N N O O O O O |
| FISGUJ10 | 0.035 | 1.00 | 1.32 | 0.319 | ****** | O N N O O O O O |
| GACDAP | 0.074 | 1.00 | 1.06 | 0.058 | | O N O N O O O O |
| GAHLIK | 0.085 | 1.00 | 1.02 | 0.016 | | O N N O O O O O |
| GAHLIK | 0.085 | 1.00 | 1.07 | 0.066 | | O N N O O O O O |
| GAZGIX | 0.032 | 1.00 | 1.04 | 0.044 | | O N N O O O O O |
| GEPZEG | 0.038 | 1.00 | 1.06 | 0.065 | | O N N O O O O O |
| GESSEC | 0.121 | 1.00 | 0.97 | -0.031 | | O N N O O O O O |
| GESSEC | 0.121 | 1.00 | 1.08 | 0.084 | | O N N O O O O O |
| GESSEC | 0.121 | 1.00 | 1.12 | 0.125 | | O N N O O O O O |
| GESSEC | 0.121 | 1.00 | 1.05 | 0.052 | | O N N O O O O O |
| HARLAN | 0.051 | 1.00 | 1.11 | 0.108 | | O N N O O O O O |
| HARLAN | 0.051 | 1.00 | 1.07 | 0.069 | | O N N O O O O O |
| HASTEA | 0.067 | 1.00 | 1.07 | 0.066 | | O N N O O O O O |
| JAPVEB | 0.032 | 1.00 | 1.06 | 0.062 | | O N N O O O O O |
| JECFEC[a] | 0.170 | 1.00 | 0.92 | -0.077 | | N N N N N N N N |
| JEDNIP | 0.069 | 1.00 | 1.03 | 0.027 | | O N N O O O O O |
| JIRYOY | 0.060 | 1.00 | 1.08 | 0.077 | | O N N O O O O O |
| JUYMEV | 0.030 | 1.00 | 1.10 | 0.098 | | O N N O O O O O |
| KAFJEG | 0.049 | 1.00 | 1.04 | 0.036 | | O N N O O O O O |

Appendix Table A-1 continued.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| KCRYPT10 | 0.046 | 1.00 | 1.23 | 0.225 | | O N N O O O O O |
| KEJGOV | 0.095 | 1.00 | 1.05 | 0.052 | | O N N O O O O O |
| KEJGOV | 0.095 | 1.00 | 1.06 | 0.061 | | O N N O O O O O |
| KEJGOV | 0.095 | 1.00 | 1.03 | 0.030 | | O N N O O O O O |
| KEJGOV | 0.095 | 1.00 | 1.11 | 0.113 | | O N N O O O O O |
| KINMUP | 0.079 | 1.00 | 1.04 | 0.036 | | O N N O O O O O |
| KIXWET10 | 0.040 | 1.00 | 1.08 | 0.075 | | O N N O O O O O |
| KIZLEK | 0.043 | 1.00 | 1.10 | 0.102 | | O N N O O O O O |
| KUVTAW | 0.061 | 1.00 | 1.07 | 0.069 | | O N N O O O O O |
| KUVTEA | 0.057 | 1.00 | 1.10 | 0.095 | | O N N O O O O O |
| LEFKAI01 | 0.102 | 1.00 | 1.30 | 0.303 | ****** | O N N O O O O O |
| LEFKOW | 0.077 | 1.00 | 1.07 | 0.075 | | O N N O O O O O |
| LEFKOW | 0.077 | 1.00 | 1.05 | 0.047 | | O N N O O O O O |
| LESHEW | 0.081 | 1.00 | 1.00 | 0.003 | | O N O O O O O O |
| LIBKAI | 0.017 | 1.00 | 0.96 | -0.042 | | O N O O O O O O |
| NACPUC | 0.068 | 1.00 | 1.00 | -0.004 | | O N N O O O O O |
| NAYTOW | 0.043 | 1.00 | 1.16 | 0.165 | | O N O O O O O O |
| NERWIQ | 0.095 | 1.00 | 1.04 | 0.043 | | O N N O O O O O |
| NERWIQ | 0.095 | 1.00 | 1.10 | 0.102 | | O N N O O O O O |
| NERWOW | 0.094 | 1.00 | 1.08 | 0.083 | | O N N O O O O O |
| NITDEZ | 0.046 | 1.00 | 1.10 | 0.101 | | O N N O O O O O |
| NITDEZ | 0.046 | 1.00 | 1.04 | 0.036 | | O N N O O O O O |
| NITDID | 0.049 | 1.00 | 1.07 | 0.067 | | O N N O O O O O |
| NOLXAN | 0.043 | 1.00 | 1.04 | 0.042 | | O N N O O O O O |
| NOLXAN | 0.043 | 1.00 | 1.06 | 0.058 | | O N N O O O O O |
| NOLXER | 0.079 | 1.00 | 1.06 | 0.064 | | O N N O O O O O |
| NOLXER | 0.079 | 1.00 | 1.12 | 0.122 | | O N N O O O O O |
| NOLXER | 0.079 | 1.00 | 1.06 | 0.065 | | O N N O O O O O |
| NOLXIV | 0.095 | 1.00 | 1.15 | 0.151 | | O N N O O O O O |
| NOLXIV | 0.095 | 1.00 | 1.09 | 0.087 | | O N N O O O O O |
| NOLXIV | 0.095 | 1.00 | 1.05 | 0.051 | | O N N O O O O O |
| NUQWUR | 0.053 | 1.00 | 1.00 | -0.001 | | O N O N O O O O |
| PIBWUS | 0.051 | 1.00 | 1.04 | 0.041 | | O N N O O O O O |
| POHPUX | 0.103 | 1.00 | 1.08 | 0.078 | | O N N O O O O O |
| POHPUX | 0.103 | 1.00 | 0.98 | -0.017 | | O N N O O O O O |
| POHPUX | 0.103 | 1.00 | 1.02 | 0.018 | | O N N O O O O O |
| POHRAF | 0.068 | 1.00 | 1.03 | 0.025 | | O N N O O O O O |
| POHRAF | 0.068 | 1.00 | 1.02 | 0.016 | | O N N O O O O O |
| POHRAF | 0.068 | 1.00 | 1.17 | 0.173 | | O N N O O O O O |
| POJFID | 0.046 | 1.00 | 1.04 | 0.039 | | O N N O O O O O |
| POJFID | 0.046 | 1.00 | 1.03 | 0.028 | | O N N O O O O O |
| PULVAT | 0.048 | 1.00 | 1.08 | 0.077 | | O N N O O O O O |

Appendix Table A-1 continued.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| RASCIX | 0.048 | 1.00 | 1.12 | 0.116 | | O N O O O O O O |
| REJQIG | 0.063 | 1.00 | 1.08 | 0.079 | | O N N O O O O O |
| REJQIG | 0.063 | 1.00 | 1.09 | 0.094 | | O N N O O O O O |
| REJQIG | 0.063 | 1.00 | 1.11 | 0.112 | | O N N O O O O O |
| RERYUI | 0.030 | 1.00 | 1.03 | 0.035 | | O N N O O O O O |
| RERYUI | 0.030 | 1.00 | 1.07 | 0.067 | | O N N O O O O O |
| RINRAH | 0.052 | 1.00 | 1.09 | 0.090 | | O N N O O O O O |
| RINRIP | 0.060 | 1.00 | 1.05 | 0.049 | | O N N O O O O O |
| RINRIP | 0.060 | 1.00 | 1.01 | 0.010 | | O N N O O O O O |
| RIQYAR | 0.055 | 1.00 | 1.01 | 0.015 | | O N N O O O O O |
| RIQYAR | 0.055 | 1.00 | 1.11 | 0.115 | | O N N O O O O O |
| RIQYAR | 0.055 | 1.00 | 1.08 | 0.076 | | O N N O O O O O |
| RIQYEV | 0.105 | 1.00 | 1.23 | 0.225 | | O N N O O O O O |
| RIQYEV | 0.105 | 1.00 | 1.25 | 0.252 | | O N N O O O O O |
| RIXPOD | 0.043 | 1.00 | 1.11 | 0.109 | | O N N O O O O O |
| RIXPOD | 0.043 | 1.00 | 1.06 | 0.060 | | O N N O O O O O |
| SAHYOP | 0.029 | 1.00 | 1.07 | 0.067 | | O N N O O O O O |
| SILRAG | 0.051 | 1.00 | 0.99 | -0.012 | | O N O O O O O N |
| SOCSIM10 | 0.057 | 1.00 | 1.04 | 0.039 | | O N N O O O O O |
| SOGGAW10 | 0.083 | 1.00 | 1.04 | 0.039 | | O N N O O O O O |
| SOGGAW10 | 0.083 | 1.00 | 1.14 | 0.144 | | O N N O O O O O |
| SOGGAW10 | 0.083 | 1.00 | 1.04 | 0.036 | | O N N O O O O O |
| TAHQEY | 0.063 | 1.00 | 1.17 | 0.168 | | O N N O O O O O |
| TAHQEY | 0.063 | 1.00 | 1.21 | 0.206 | | O N N O O O O O |
| TAHQIC | 0.082 | 1.00 | 0.95 | -0.053 | | O N N O O O O O |
| TAHQIC | 0.082 | 1.00 | 1.09 | 0.090 | | O N N O O O O O |
| TAVDUP | 0.040 | 1.00 | 1.08 | 0.076 | | O N N O O O O O |
| TAVFAX | 0.117 | 1.00 | 1.08 | 0.076 | | O N N O O O O O |
| TAVFEB | 0.055 | 1.00 | 1.16 | 0.163 | | O N N O O O O O |
| TAVFEB | 0.055 | 1.00 | 1.06 | 0.056 | | O N N O O O O O |
| TAVFIF | 0.055 | 1.00 | 1.09 | 0.089 | | O N N O O O O O |
| TAVFIF | 0.055 | 1.00 | 1.13 | 0.127 | | O N N O O O O O |
| TIQQOZ | 0.105 | 1.00 | 1.03 | 0.034 | | O N N O O O O O |
| TIQQOZ | 0.105 | 1.00 | 1.04 | 0.035 | | O N N O O O O O |
| TISROC | 0.032 | 1.00 | 1.05 | 0.048 | | O N N O O O O O |
| TOCYUF | 0.039 | 1.00 | 1.02 | 0.020 | | O N N O O O O O |
| TOCYUF | 0.039 | 1.00 | 1.00 | 0.000 | | O N N O O O O O |
| TOCZAM | 0.040 | 1.00 | 1.07 | 0.068 | | O N N O O O O O |
| TOCZAM | 0.040 | 1.00 | 1.07 | 0.073 | | O N N O O O O O |
| TUBNEJ | 0.051 | 1.00 | 1.36 | 0.364 | ****** | O N N O O O O O |
| TUKCUX | 0.103 | 1.00 | 1.37 | 0.372 | ****** | O N N O O O O O |
| TUPCAI | 0.069 | 1.00 | 1.05 | 0.054 | | O N N O O O O O |

Appendix Table A-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| TUPCEM | 0.117 | 1.00 | 1.08 | 0.084 | O N N O O O O O |
| TUPCEM | 0.117 | 1.00 | 1.06 | 0.058 | O N N O O O O O |
| TUPCIQ | 0.085 | 1.00 | 1.04 | 0.044 | O N N O O O O O |
| TUPCIQ | 0.085 | 1.00 | 1.06 | 0.063 | O N N O O O O O |
| TUPCOW | 0.064 | 1.00 | 1.03 | 0.026 | O N N O O O O O |
| TUPCOW | 0.064 | 1.00 | 1.04 | 0.043 | O N N O O O O O |
| TUPCOW | 0.064 | 1.00 | 1.07 | 0.072 | O N N O O O O O |
| TUPCOW | 0.064 | 1.00 | 1.18 | 0.178 | O N N O O O O O |
| TUPSOM | 0.055 | 1.00 | 1.03 | 0.030 | O N N O O O O O |
| TUQTAA | 0.109 | 1.00 | 0.96 | -0.035 | O N N O O O O O |
| TUQTAA | 0.109 | 1.00 | 1.12 | 0.119 | O N N O O O O O |
| VERKEI | 0.064 | 1.00 | 0.99 | -0.009 | O N N O O O O O |
| VERKEI | 0.064 | 1.00 | 0.97 | -0.028 | O N N O O O O O |
| VERKEI | 0.064 | 1.00 | 1.17 | 0.169 | O N N O O O O O |
| VERKEI | 0.064 | 1.00 | 1.09 | 0.088 | O N N O O O O O |
| VIKFIE | 0.039 | 1.00 | 1.09 | 0.092 | O N N O O O O O |
| VUYZEU | 0.042 | 1.00 | 1.05 | 0.053 | O N O O O O O N |
| WADBUY | 0.053 | 1.00 | 1.05 | 0.051 | O N N O O O O O |
| WAVFII | 0.087 | 1.00 | 1.04 | 0.037 | O N N O O O O O |
| WAVFII | 0.087 | 1.00 | 1.09 | 0.093 | O N N O O O O O |
| WAVFII | 0.087 | 1.00 | 1.04 | 0.042 | O N N O O O O O |
| WEKBET | 0.043 | 1.00 | 1.19 | 0.191 | O N N N N O O O |
| YAHLAU | 0.082 | 1.00 | 1.18 | 0.183 | O N O O O O O O |
| YEKMAC | 0.029 | 1.00 | 1.04 | 0.040 | O N N O O O O O |
| YEKMAC | 0.029 | 1.00 | 1.06 | 0.059 | O N N O O O O O |
| YENBIC11 | 0.067 | 1.00 | 1.02 | 0.018 | O N N O O O O O |
| YENBIC11 | 0.067 | 1.00 | 1.06 | 0.061 | O N N O O O O O |
| YENBIC11 | 0.067 | 1.00 | 1.01 | 0.009 | O N N O O O O O |
| YENBIC11 | 0.067 | 1.00 | 1.04 | 0.039 | O N N O O O O O |
| YENBIC11 | 0.067 | 1.00 | 0.95 | -0.051 | O N N O O O O O |
| YENBIF10 | 0.060 | 1.00 | 1.05 | 0.048 | O N N O O O O O |
| YENBIF10 | 0.060 | 1.00 | 1.04 | 0.044 | O N N O O O O O |
| YENBIF10 | 0.060 | 1.00 | 1.05 | 0.050 | O N N O O O O O |
| YENBIF10 | 0.060 | 1.00 | 1.05 | 0.046 | O N N O O O O O |
| YENBIF10 | 0.060 | 1.00 | 1.07 | 0.067 | O N N O O O O O |
| YENBIF10 | 0.060 | 1.00 | 1.00 | -0.002 | O N N O O O O O |
| YENBOI | 0.102 | 1.00 | 1.02 | 0.016 | O N N O O O O O |
| YENBOI | 0.102 | 1.00 | 1.04 | 0.042 | O N N O O O O O |
| YENBOI | 0.102 | 1.00 | 1.08 | 0.077 | O N N O O O O O |
| YUVGAX | 0.042 | 1.00 | 1.09 | 0.093 | O N N O O O O O |
| YUVGAX | 0.042 | 1.00 | 1.06 | 0.058 | O N N O O O O O |
| ZIMSUJ | 0.045 | 1.00 | 1.07 | 0.068 | O N N O O O O O |

Appendix Table A-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| ZIMSUJ | 0.045 | 1.00 | 1.03 | 0.028 | O N N O O O O O |
| ZIMSUJ | 0.045 | 1.00 | 1.04 | 0.039 | O N N O O O O O |
| ZIMTAQ | 0.111 | 1.00 | 1.09 | 0.092 | O N N O O O O O |
| ZIMTAQ | 0.111 | 1.00 | 1.04 | 0.043 | O N N O O O O O |
| ZIMTAQ | 0.111 | 1.00 | 1.06 | 0.058 | O N N O O O O O |
| ZIQYUT | 0.070 | 1.00 | 1.09 | 0.087 | O N N O O O O O |
| ZIQYUT | 0.070 | 1.00 | 1.06 | 0.065 | O N N O O O O O |
| ZIQYUT | 0.070 | 1.00 | 1.06 | 0.063 | O N N O O O O O |
| ZIQYUT | 0.070 | 1.00 | 1.08 | 0.077 | O N N O O O O O |
| ZIRLER | 0.074 | 1.00 | 1.14 | 0.136 | O N N O O O O O |
| ZIRLER | 0.074 | 1.00 | 1.30 | 0.296 | O N N O O O O O |
| ZURJAX | 0.068 | 1.00 | 1.09 | 0.093 | O N N O O O O O |
| ZURJEB | 0.057 | 1.00 | 1.09 | 0.087 | O N N O O O O O |

Note: REFCODE is the reference code used in the CSD file, Rval is the usual crystallographic *R* value found in the CSD file, Ox is the oxidation state of the Na atom, BVS is the bond valence sum calculated using the $R_0$ value of 2.105 Å. for K-N, Del is the difference between Ox and BVS and entries where Del is > 0.30 are marked with ******, Donor Atoms is the number and type of donor atoms coordinated to the metal cation.

a These Complexes were originally listed in the CSD with CNs that were lower. New BVS values were calculated for these complexes with their adjusted and higher CNs.

Appendix Table A-2. A listing of the BVS for the 33 $KO_nN_m$ complexes which were not used in the determination of K-N $R_0$ of 2.105 Å.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| **Coordination Number 3** | | | | | | |
| GINMEV | 1.068 | 1.00 | 0.52 | -0.481 | ****** | N N N |
| GINMEV | 1.068 | 1.00 | 0.51 | -0.492 | ****** | N N N |
| GINMEV | 1.068 | 1.00 | 0.51 | -0.493 | ****** | N N N |
| GINMEV | 1.068 | 1.00 | 0.50 | -0.498 | ****** | N N N |
| HIXGOK | 1.062 | 1.00 | 0.41 | -0.587 | ****** | N N N |
| PONYOG | 1.099 | 1.00 | 0.56 | -0.436 | ****** | N O N |
| REMGEV | 1.078 | 1.00 | 0.48 | -0.521 | ****** | N N N |
| SAMMEY | 1.089 | 1.00 | 0.50 | -0.497 | ****** | N N O |
| WEHBIU | 1.034 | 1.00 | 0.16 | -0.844 | ****** | N N N |
| **Coordination Number 4** | | | | | | |
| GAQTOH | 1.091 | 1.00 | 0.55 | -0.455 | ****** | N O O N |
| GAQTOH | 1.091 | 1.00 | 0.58 | -0.420 | ****** | N O O N |
| GINMEV | 1.068 | 1.00 | 0.48 | -0.518 | ****** | N N N N |
| GINMEV | 1.068 | 1.00 | 0.46 | -0.538 | ****** | N N N N |
| JOQFIE | 1.023 | 1.00 | 0.57 | -0.434 | ****** | N O O N |
| KIYZIB | 1.057 | 1.00 | 0.43 | -0.570 | ****** | N N N N |
| NIMSEH | 1.057 | 1.00 | 0.81 | -0.192 | | N O O O |
| NIMSEH | 1.057 | 1.00 | 0.79 | -0.211 | | N O O N |
| PONYOG | 1.099 | 1.00 | 0.65 | -0.350 | ****** | N N O O |
| RAFSUM | 1.026 | 1.00 | 0.60 | -0.402 | ****** | N N N N |
| REMGEV | 1.078 | 1.00 | 0.59 | -0.411 | ****** | N N N N |
| VOHXUL | 1.052 | 1.00 | 0.63 | -0.367 | ****** | N N N O |
| ZEDVIN | 1.072 | 1.00 | 0.50 | -0.499 | ****** | N O O N |
| ZEDVIN | 1.072 | 1.00 | 0.50 | -0.497 | ****** | N O O N |
| ZEDVIN | 1.072 | 1.00 | 0.51 | -0.487 | ****** | N O O N |
| ZUBGOS | 1.069 | 1.00 | 1.82 | 0.816 | ****** | N N O O |
| **Coordination Number 5** | | | | | | |
| SARHUO | 1.065 | 1.00 | 0.66 | -0.342 | ****** | N N O N N |
| WECXIL | 1.029 | 1.00 | 0.58 | -0.416 | ****** | N N N O O |

Appendix Table A-2 continued.

| REFCODE | Rval | Ox | BVS | Del |  | Donor Atoms |
|---|---|---|---|---|---|---|
| **Coordination Number 6** |  |  |  |  |  |  |
| NITFAX | 1.066 | 1.00 | 0.61 | -0.392 | ****** | N N N N N N |
| POPVEV | 1.050 | 1.00 | 2.07 | 1.068 | ****** | N N N N N N |
| POPVEV | 1.050 | 1.00 | 2.07 | 1.068 | ****** | N N N N N N |
| **Coordination Number 7** |  |  |  |  |  |  |
| WEHBIU | 1.034 | 1.00 | 0.44 | -0.560 | ****** | N N N N N N N |
| **Coordination Number 8** |  |  |  |  |  |  |
| CICDEX | 1.062 | 1.00 | 1.46 | 0.459 | ****** | O N N N N O O O |
| COYDEZ | 1.095 | 1.00 | 2.11 | 1.106 | ****** | O N N O O O O O |

Note: REFCODE is the reference code used in the CSD file, Rval is the usual crystallographic R value found in the CSD file, Ox is the oxidation state of the Na atom, BVS is the bond valence sum calculated using the $R_0$ value of 2.105 Å. for K-N, Del is the difference between Ox and BVS, Donor Atoms is the number and type of donor atoms coordinated to the metal cation. Entries where del is > 0.3 valence units are marked with ******

# APPENDIX B
# LIST OF NA-O,N COMPLEXES USED FOR THE BVS ANALYSIS

Appendix Table B-1. A listing of the BVS for the 244 $NaO_nN_m$ (n = 0-6, m = 1-7) complexes used in the determination of Na-N $R_0$ of 1.935 Å.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| **Coordination Number 3** | | | | | | |
| HADYOA | 0.055 | 1.00 | 0.77 | -0.225 | | N O O |
| JOGFOA | 0.055 | 1.00 | 0.89 | -0.109 | | N N O |
| JONVUD | 0.103 | 1.00 | 1.03 | 0.034 | | N N N |
| JONVUD | 0.103 | 1.00 | 1.17 | 0.165 | | N N N |
| NEXKOQ | 0.095 | 1.00 | 0.89 | -0.106 | | N N N |
| NEXKOQ | 0.095 | 1.00 | 0.90 | -0.097 | | N N N |
| NUWBUC | 0.076 | 1.00 | 0.72 | -0.278 | | N N N |
| SUJQUJ | 0.030 | 1.00 | 0.57 | –0.429 | ****** | N O N |
| VESSAN | 0.029 | 1.00 | 0.91 | -0.091 | | N N N |
| VOVGUI | 0.046 | 1.00 | 0.87 | -0.128 | | N N O |
| WASWOC | 1.055 | 1.00 | 0.71 | -0.287 | | N N O |
| **Coordination Number 4** | | | | | | |
| BIPJIT10 | 0.050 | 1.00 | 0.78 | -0.220 | | N N N N |
| BIPJIT20 | 0.041 | 1.00 | 0.79 | -0.215 | | N N N N |
| DUYTOG | 0.062 | 1.00 | 1.10 | 0.102 | | N N N O |
| DUYTOG | 0.062 | 1.00 | 1.07 | 0.070 | | N N N O |
| DUYTOG | 0.062 | 1.00 | 1.00 | 0.003 | | N N N O |
| FAQGAF | 0.044 | 1.00 | 0.74 | -0.262 | | N N O O |
| GIDQEP | 0.046 | 1.00 | 1.05 | 0.054 | | N N O O |
| HIWQOT | 0.082 | 1.00 | 0.84 | -0.160 | | N O N N |
| HIWQOT | 0.082 | 1.00 | 0.78 | -0.217 | | N O O O |
| JEPWAC | 0.036 | 1.00 | 0.96 | -0.036 | | N N N N |
| JEYXOA | 0.070 | 1.00 | 0.99 | -0.012 | | N O O O |
| JIRGIA | 0.068 | 1.00 | 0.72 | -0.282 | | N N N N |
| JONVUD | 0.103 | 1.00 | 0.96 | -0.039 | | N N N N |
| JONVUD | 0.103 | 1.00 | 0.98 | -0.023 | | N N N N |
| KABYOB | 0.046 | 1.00 | 1.01 | 0.015 | | N N N N |

Appendix Table B-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| KEBHOO | 0.060 | 1.00 | 1.02 | 0.015 | N O O O |
| KORLAE | 0.051 | 1.00 | 1.20 | 0.203 | N N N N |
| NANNAR | 0.044 | 1.00 | 0.79 | -0.210 | N O O O |
| NEXKOQ | 0.095 | 1.00 | 0.85 | -0.155 | N N N N |
| NEXKUW | 0.127 | 1.00 | 0.94 | -0.062 | N N N N |
| NEXKUW | 0.127 | 1.00 | 1.04 | 0.041 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.92 | -0.080 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.90 | -0.099 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.91 | -0.092 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.87 | -0.129 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.91 | -0.092 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.92 | -0.081 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.80 | -0.198 | N N N N |
| NOMPAG | 0.076 | 1.00 | 0.82 | -0.176 | N N N N |
| PAFQOC | 0.067 | 1.00 | 0.91 | -0.088 | N N N N |
| PAZTUF | 0.042 | 1.00 | 0.87 | -0.132 | N O O O |
| PAZTUF | 0.042 | 1.00 | 0.85 | -0.154 | N O O O |
| PEJROL | 0.093 | 1.00 | 1.10 | 0.097 | N N N N |
| REMGUL | 0.096 | 1.00 | 1.02 | 0.018 | N O O O |
| REMGUL | 0.096 | 1.00 | 1.04 | 0.044 | N O O O |
| RILLAZ | 0.107 | 1.00 | 1.01 | 0.009 | N O O O |
| RILMEE | 0.098 | 1.00 | 0.99 | -0.013 | N N O O |
| RILMII | 0.169 | 1.00 | 0.91 | -0.091 | N N N N |
| ROPLIR | 0.072 | 1.00 | 0.82 | -0.177 | N O O O |
| SADXOK | 0.059 | 1.00 | 0.86 | -0.142 | N N N N |
| SAMMOI | 0.062 | 1.00 | 0.95 | -0.048 | N N O O |
| SARHIC | 0.076 | 1.00 | 0.96 | -0.039 | N N O N |
| SARHOI | 0.086 | 1.00 | 0.93 | -0.070 | N N O O |
| SARHOI | 0.086 | 1.00 | 0.91 | -0.093 | N N N N |
| SEKCIU10 | 0.032 | 1.00 | 1.12 | 0.117 | N O O N |
| SILZAO | 0.065 | 1.00 | 0.92 | -0.078 | N O N N |
| SILZAO | 0.065 | 1.00 | 0.94 | -0.056 | N O N N |
| TERKEG | 0.048 | 1.00 | 0.82 | -0.178 | N O O O |
| TIBVIJ | 0.042 | 1.00 | 0.97 | -0.027 | N N N N |
| TIVPUJ | 0.043 | 1.00 | 0.82 | -0.184 | N N N N |
| TIVPUJ | 0.043 | 1.00 | 0.82 | -0.185 | N N N N |
| TIVQAQ | 0.053 | 1.00 | 0.83 | -0.174 | N N N N |
| TIVQAQ | 0.053 | 1.00 | 0.84 | -0.158 | N N N N |
| TOJXEV | 0.051 | 1.00 | 0.78 | -0.225 | N N N O |
| VAKDAM | 0.059 | 1.00 | 0.96 | -0.043 | N O O N |
| VAKDAM | 0.059 | 1.00 | 1.00 | -0.005 | N O O N |
| VAVZIB | 0.027 | 1.00 | 1.03 | 0.027 | N N N N |

Appendix Table B-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| VAVZIB | 0.027 | 1.00 | 0.95 | -0.049 | N N N N |
| VAVZOH | 0.032 | 1.00 | 1.03 | 0.028 | N N N O |
| VAVZOH | 0.032 | 1.00 | 1.06 | 0.059 | N N N O |
| VESTIW | 0.048 | 1.00 | 1.05 | 0.046 | N N N N |
| VOHXOF | 0.043 | 1.00 | 0.90 | -0.103 | N N N O |
| VOHXOF | 0.043 | 1.00 | 0.94 | -0.064 | N N N O |
| VOVGOC | 0.056 | 1.00 | 0.74 | -0.255 | N N O O |
| WECXEH | 0.023 | 1.00 | 0.93 | -0.074 | N N O O |
| WEHBAM | 0.033 | 1.00 | 0.81 | -0.186 | N N N N |
| YAKTIN | 0.076 | 1.00 | 1.14 | 0.144 | N N N N |
| YANRIO | 0.059 | 1.00 | 0.90 | -0.097 | N O O O |
| YIXYEJ | 0.055 | 1.00 | 0.92 | -0.080 | N N N N |
| YOZJOM | 0.047 | 1.00 | 0.96 | -0.040 | N O O N |

**Coordination Number 5**

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| GEVQIH | 0.051 | 1.00 | 0.85 | -0.148 | N O O O O |
| HEWXOW | 0.054 | 1.00 | 1.03 | 0.032 | N N N N N |
| HIDCOM | 0.051 | 1.00 | 1.00 | -0.005 | N O O O N |
| HIJVAX | 0.154 | 1.00 | 0.99 | -0.006 | N O O O N |
| HIJVAX | 0.154 | 1.00 | 0.94 | -0.064 | N O O O N |
| JEHHUZ | 0.097 | 1.00 | 0.98 | -0.020 | N O O O O |
| KIJKAP | 0.051 | 1.00 | 1.04 | 0.044 | N O O O N |
| KIJKAP | 0.051 | 1.00 | 1.06 | 0.062 | N O O O N |
| KISSUA | 0.031 | 1.00 | 1.07 | 0.070 | N O O O N |
| LEXDEX | 0.070 | 1.00 | 0.94 | -0.059 | N N N N O |
| NANBOT | 0.048 | 1.00 | 1.03 | 0.033 | N N O O O |
| NANBUZ | 0.051 | 1.00 | 1.00 | -0.001 | N N O O O |
| NUPRUL | 0.065 | 1.00 | 0.98 | -0.019 | N O O O O |
| PESTEM | 0.042 | 1.00 | 1.10 | 0.100 | N O O O O |
| PETZET | 0.061 | 1.00 | 1.13 | 0.126 | N N N N N |
| PETZET | 0.061 | 1.00 | 1.14 | 0.144 | N N N N N |
| PETZET | 0.061 | 1.00 | 1.09 | 0.089 | N N N N N |
| PETZET | 0.061 | 1.00 | 1.11 | 0.107 | N N N N N |
| POGDAQ | 0.067 | 1.00 | 1.05 | 0.053 | N O O O O |
| PUTRUR | 0.034 | 1.00 | 1.07 | 0.071 | N O O O N |
| PUTSAY | 0.053 | 1.00 | 1.05 | 0.051 | N O O O N |
| PUTSEC | 0.052 | 1.00 | 0.96 | -0.036 | N O O O O |
| PUTSIG | 0.044 | 1.00 | 0.93 | -0.068 | N O O O O |
| RACRUI | 0.042 | 1.00 | 1.02 | 0.018 | N O O O O |
| RILMII | 0.169 | 1.00 | 1.16 | 0.159 | N N N N N |

Appendix Table B-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| RUHRAN | 0.077 | 1.00 | 1.29 | 0.292 | N N N N O |
| SOWYIM10 | 0.043 | 1.00 | 0.83 | -0.171 | N O O O O |
| SOYZOV | 0.074 | 1.00 | 0.97 | -0.034 | N N N N O |
| SUMFUB | 0.034 | 1.00 | 1.18 | 0.176 | N N O O N |
| VAKDIU | 0.021 | 1.00 | 0.91 | -0.093 | N O O O O |
| VAKDIU | 0.021 | 1.00 | 0.98 | -0.025 | N O O O O |
| VESTOC | 0.085 | 1.00 | 0.96 | -0.035 | N N N N N |
| YOYCEU | 0.065 | 1.00 | 1.06 | 0.060 | N N N N N |
| ZUBKAI | 0.077 | 1.00 | 1.13 | 0.127 | N O O N O |
| ZUBKAI | 0.077 | 1.00 | 1.09 | 0.094 | N O O N O |
| ZUDMIU | 0.060 | 1.00 | 1.05 | 0.048 | N N O O O |

**Coordination Number 6**

| | | | | | | |
|---|---|---|---|---|---|---|
| BAGTUY | 0.056 | 1.00 | 0.90 | -0.103 | | N N O O O O |
| BOBBAV | 0.060 | 1.00 | 1.14 | 0.142 | | N O O O O O |
| BOYRIQ | 0.037 | 1.00 | 1.09 | 0.093 | | N O O O O O |
| CEPKUD | 0.070 | 1.00 | 1.10 | 0.097 | | N O O O O O |
| CIJMOX | 0.100 | 1.00 | 0.92 | -0.080 | | N O O O O O |
| CORNEC | 0.045 | 1.00 | 0.85 | -0.152 | | N O O O O O |
| DORSUY | 0.039 | 1.00 | 1.24 | 0.238 | | N N O O O N |
| GIJMOB | 0.079 | 1.00 | 1.24 | 0.238 | | N O O O O O |
| GIXBAQ | 0.046 | 1.00 | 1.14 | 0.145 | | N O O N N N |
| GOCVEZ | 0.025 | 1.00 | 0.93 | -0.074 | | N O O O O O |
| HIXNEH | 1.054 | 1.00 | 1.31 | 0.306 | ****** | N N N N N N |
| JILXUX | 0.086 | 1.00 | 1.20 | 0.198 | | N N O O O O |
| JOKFIY | 0.033 | 1.00 | 1.25 | 0.248 | | N N N N N N |
| KIPDOC | 0.033 | 1.00 | 0.92 | -0.085 | | N O O O O O |
| KORKUX | 0.040 | 1.00 | 1.25 | 0.248 | | N O O O O O |
| KUNYEX | 0.043 | 1.00 | 1.14 | 0.142 | | N O O O O O |
| LIHPAT | 0.041 | 1.00 | 0.74 | -0.258 | | N O O O N N |
| NANBAF | 0.041 | 1.00 | 1.13 | 0.128 | | N O O O O O |
| NANBAF | 0.041 | 1.00 | 1.11 | 0.115 | | N O O O O O |
| NANBEJ | 0.053 | 1.00 | 1.10 | 0.097 | | N O O O O O |
| NANBIN | 0.040 | 1.00 | 0.94 | -0.058 | | N N O O O O |
| NOKGEZ | 0.045 | 1.00 | 0.90 | -0.099 | | N O O O O O |
| NOPSUG | 0.051 | 1.00 | 0.89 | -0.107 | | N O O O O O |
| NOSPIU | 0.041 | 1.00 | 1.17 | 0.167 | | N O O O O N |
| PAGVIC | 0.045 | 1.00 | 1.17 | 0.170 | | N N N N O O |
| PATFOF | 0.059 | 1.00 | 1.08 | 0.079 | | N O O O O O |

Appendix Table B-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| PIZSIA | 0.058 | 1.00 | 1.03 | 0.026 | N O O O O O |
| POGZAM | 0.078 | 1.00 | 1.18 | 0.177 | N O O O O O |
| PUGKEH | 0.053 | 1.00 | 1.28 | 0.282 | N O O N N O |
| PUTSAY | 0.053 | 1.00 | 1.16 | 0.156 | N O O O O N |
| PUTSUS | 0.048 | 1.00 | 1.02 | 0.017 | N O O O O O |
| PUTSUS | 0.048 | 1.00 | 1.00 | -0.001 | N O O O O O |
| RECMIV01 | 0.026 | 1.00 | 0.92 | -0.078 | N O O O O O |
| RILMEE | 0.098 | 1.00 | 1.15 | 0.149 | N N N N O O |
| SAJJES | 0.042 | 1.00 | 1.05 | 0.053 | N O O O O O |
| SIBCOV | 0.038 | 1.00 | 0.98 | -0.017 | N O O O O O |
| SOJCOJ | 0.037 | 1.00 | 1.30 | 0.297 | N O O O O O |
| SOYZUB | 0.064 | 1.00 | 1.23 | 0.230 | N N N N N N |
| TAHRID | 0.056 | 1.00 | 0.86 | -0.139 | N O N O O O |
| TATTAJ01 | 0.030 | 1.00 | 1.10 | 0.095 | N N N N N N |
| TIVJAJ | 0.043 | 1.00 | 1.25 | 0.251 | N O O O O N |
| TOZPED | 0.056 | 1.00 | 1.02 | 0.018 | N O O O O O |
| VARZIX | 0.048 | 1.00 | 1.14 | 0.140 | N O O O O O |
| YAHKIB | 0.076 | 1.00 | 1.05 | 0.051 | N N O O O O |
| YAHKUN | 0.043 | 1.00 | 0.97 | -0.026 | N O O O O N |

**Coordination Number 7**

| | | | | | |
|---|---|---|---|---|---|
| BIVNEZ | 0.030 | 1.00 | 1.15 | 0.146 | N N N N O O O |
| BIZTOT | 0.046 | 1.00 | 1.09 | 0.091 | N N O O O O O |
| BUKBAK | 0.084 | 1.00 | 1.05 | 0.055 | N O O O O O O |
| CESRAT | 0.054 | 1.00 | 0.92 | -0.079 | N O O O O O N |
| CESRAT | 0.054 | 1.00 | 0.97 | -0.032 | N O O O O O N |
| DUFZOT01 | 0.117 | 1.00 | 1.22 | 0.222 | N N O O O O O |
| FIDDUR | 0.035 | 1.00 | 1.14 | 0.140 | N O O O O O O |
| GOCVID | 0.035 | 1.00 | 0.97 | -0.033 | N O O O O O N |
| HEDXOD | 0.060 | 1.00 | 0.99 | -0.005 | N N O O O O O |
| HEXWUC | 0.045 | 1.00 | 1.16 | 0.163 | N O O O O O O |
| HEXXEN | 0.041 | 1.00 | 1.15 | 0.152 | N O O O O O O |
| JUQPAM | 0.040 | 1.00 | 1.09 | 0.088 | N O O O O O N |
| JUQPAM | 0.040 | 1.00 | 1.23 | 0.231 | N O O O O O N |
| JUQPEQ | 0.060 | 1.00 | 1.03 | 0.031 | N O O O O O N |
| KARFIS | 0.078 | 1.00 | 1.05 | 0.047 | N O O O O O O |
| NOSPIU | 0.041 | 1.00 | 1.07 | 0.067 | N O O O O O O |
| PEHMAQ | 0.041 | 1.00 | 1.00 | -0.001 | N O O O O O O |
| PEHPIB | 0.062 | 1.00 | 1.18 | 0.176 | N O O O O O O |
| POZTNA | 0.046 | 1.00 | 1.00 | 0.002 | N N O O O O O |
| ROQSOF | 0.050 | 1.00 | 1.13 | 0.133 | N O O O O O O |

Appendix Table B-1 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| RURYOS | 0.083 | 1.00 | 0.99 | -0.010 | N N O O O O O |
| RUVMAW | 0.047 | 1.00 | 1.07 | 0.072 | N O O O O O O |
| SOGYOC | 0.053 | 1.00 | 1.02 | 0.023 | N N O O O O O |
| SULJAK | 0.048 | 1.00 | 1.20 | 0.200 | N O O O O O N |
| SULJAK | 0.048 | 1.00 | 1.18 | 0.181 | N N O O O O O |
| TERLAD | 0.088 | 1.00 | 0.75 | -0.253 | N O O O O O O |
| TONHUZ | 0.043 | 1.00 | 1.12 | 0.124 | N O O O O O O |
| YAGWEI | 0.091 | 1.00 | 1.16 | 0.159 | N N O O O O O |
| YAVCIH | 0.031 | 1.00 | 1.12 | 0.115 | N O O O O O O |
| YURFOG | 0.090 | 1.00 | 1.01 | 0.006 | N N O O O O O |
| ZAWKOX | 0.051 | 1.00 | 1.19 | 0.186 | N N N O O O O |
| ZOHYIE | 0.042 | 1.00 | 1.04 | 0.041 | N O O O O O O |
| ZOMBAE | 0.046 | 1.00 | 0.73 | -0.273 | N O O O O O O |
| REGTEC[a] | 0.036 | 1.00 | 0.95 | -0.049 | N O O O O O O |

**Coordination Number 8**

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| BIGPIQ | 0.050 | 1.00 | 0.77 | -0.231 | N N O O O O O O |
| CEJCUP | 0.028 | 1.00 | 1.05 | 0.047 | N N O O O O O O |
| CPNASN | 0.086 | 1.00 | 0.74 | -0.263 | N N O O O O O O |
| CPNASN | 0.086 | 1.00 | 0.93 | -0.069 | N N O O O O O O |
| CRNAPB10 | 0.086 | 1.00 | 0.85 | -0.155 | N N O O O O O O |
| DEDZOB | 0.047 | 1.00 | 0.94 | -0.062 | N N O O O O O O |
| DEWGIV | 0.082 | 1.00 | 0.81 | -0.189 | N N O O O O O O |
| DEWGIV | 0.082 | 1.00 | 1.04 | 0.041 | N N O O O O O O |
| HAYDIU | 0.081 | 1.00 | 1.17 | 0.173 | N N O O O O O O |
| HAYDIU | 0.081 | 1.00 | 1.04 | 0.044 | N N O O O O O O |
| HAYDIU | 0.081 | 1.00 | 1.01 | 0.007 | N N O O O O O O |
| HEBXAN | 0.042 | 1.00 | 0.96 | -0.037 | N N O O O O O O |
| HIJNOD | 0.055 | 1.00 | 1.03 | 0.034 | N N O O O O O O |
| HIJNOD | 0.055 | 1.00 | 0.93 | -0.068 | N N O O O O O O |
| JEFMIQ | 0.103 | 1.00 | 1.17 | 0.170 | N O O O O N N N |
| JEFMIQ | 0.103 | 1.00 | 1.12 | 0.120 | N O O O O N N N |
| JEFMIQ | 0.103 | 1.00 | 1.11 | 0.108 | N O O O O N N N |
| JOLFEV | 0.088 | 1.00 | 0.89 | -0.113 | N N O O O O O O |
| JOLFEV | 0.088 | 1.00 | 0.98 | -0.023 | N N O O O O O O |
| JOLFEV | 0.088 | 1.00 | 0.93 | -0.067 | N N O O O O O O |
| KOBHOY | 0.047 | 1.00 | 1.01 | 0.014 | N N O O O O O O |
| KOBJIU | 0.071 | 1.00 | 0.91 | -0.085 | N N O O O O O O |
| KOBJUG | 0.054 | 1.00 | 0.91 | -0.086 | N N O O O O O O |
| LEHGOU | 0.041 | 1.00 | 0.89 | -0.110 | N N O O O O O O |

Appendix Table B-1 continued.

| REFCODE | Rval | Ox | BVS | Del | | Donor Atoms |
|---|---|---|---|---|---|---|
| PALYAC | 0.071 | 1.00 | 1.39 | 0.394 | ****** | N N O O O O O O |
| PALYAC | 0.071 | 1.00 | 1.38 | 0.378 | ****** | N N O O O O O O |
| PALYEG | 0.036 | 1.00 | 1.27 | 0.267 | | N N O O O O O O |
| PCFENA | 0.078 | 1.00 | 0.77 | -0.230 | | N N O O O O O O |
| POHLED | 0.073 | 1.00 | 1.26 | 0.255 | | N N N N O O O O |
| RIRQAK01 | 0.071 | 1.00 | 1.08 | 0.078 | | N N N N O O O O |
| ROQLIS | 0.042 | 1.00 | 1.11 | 0.109 | | N N O O O O O O |
| SEKZEN | 0.085 | 1.00 | 1.20 | 0.198 | | N N N N N N N N |
| SMCPCO10 | 0.060 | 1.00 | 0.83 | -0.173 | | N N O O O O O O |
| SOCSOS10 | 0.035 | 1.00 | 0.92 | -0.078 | | N N O O O O O O |
| SUDMEJ | 0.069 | 1.00 | 1.02 | 0.015 | | N N O O O O O O |
| TUBMUY | 0.056 | 1.00 | 0.94 | -0.057 | | N N O O O O O O |
| TUBNAF | 0.108 | 1.00 | 1.08 | 0.077 | | N N O O O O O O |
| TUBNOT | 0.051 | 1.00 | 1.13 | 0.130 | | N N O O O O O O |
| TUKDAE | 0.069 | 1.00 | 0.96 | -0.038 | | N N O O O O O O |
| VAFGEO | 0.065 | 1.00 | 1.02 | 0.022 | | N N N N O O O O |
| VOBSIO | 0.036 | 1.00 | 0.92 | -0.084 | | N N N N N N N N |
| VOFVER | 0.075 | 1.00 | 0.97 | -0.033 | | N N O O O O O O |
| YOBPEK | 0.058 | 1.00 | 0.84 | -0.165 | | N N O O O O O O |
| ZAWKIR | 0.072 | 1.00 | 0.95 | -0.050 | | N N O O O O O O |
| ZOGTEV | 0.073 | 1.00 | 1.05 | 0.054 | | N N O O O O O O |
| ZOGTEV | 0.073 | 1.00 | 1.09 | 0.092 | | N N O O O O O O |
| DETPIB[a] | 0.092 | 1.00 | 0.95 | -0.049 | | N N N N N N N N |
| TETJOR[a] | 0.049 | 1.00 | 0.76 | -0.235 | | N N N N O O O O |

Note: REFCODE is the reference code used in the CSD file, Rval is the usual crystallographic *R* value found in the CSD file, Ox is the oxidation state of the Na atom, BVS is the bond valence sum calculated using the $R_0$ value of 1.935 Å. for K-N, Del is the difference between Ox and BVS. Donor Atoms is the number and type of donor atoms coordinated to the metal cation. Entries where del is > 0.3 valence units are marked with ******

a These Complexes were originally listed in the CSD with CNs that were lower. New BVS values were calculated for these complexes with their adjusted and higher CNs.

Appendix Table B-2. A listing of the BVS for the 26 $NaO_nN_m$ complexes not used in the determination of Na-N $R_0$ of 1.935 Å.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| **Coordination Number 3** | | | | | |
| JUNRIT | 1.066 | 1.00 | 0.61 | -0.394 | N N N |
| JUNRIT | 1.066 | 1.00 | 0.68 | -0.320 | N N N |
| RILMII | 1.169 | 1.00 | 0.73 | -0.267 | N N N |
| SEBJUE | 1.074 | 1.00 | 0.54 | -0.458 | N N N |
| SEBJUE | 1.074 | 1.00 | 0.52 | -0.481 | N N N |
| YUPKAV | 1.089 | 1.00 | 0.60 | -0.398 | N O O |
| **Coordination Number 4** | | | | | |
| DUSVAO10 | 1.041 | 1.00 | 2.21 | 1.213 | N N N N |
| REGTEC | 1.036 | 1.00 | 0.70 | -0.299 | N O O O |
| **Coordination Number 5** | | | | | |
| KOCMUK | 1.079 | 1.00 | 1.44 | 0.440 | N O O O N |
| KOCMUK | 1.079 | 1.00 | 1.34 | 0.340 | N O O O N |
| KOCNAR | 1.071 | 1.00 | 1.23 | 0.232 | N O O O N |
| KOCNAR | 1.071 | 1.00 | 1.41 | 0.406 | N O O O N |
| KOCNAR | 1.071 | 1.00 | 1.37 | 0.366 | N O O O N |
| KOCNAR | 1.071 | 1.00 | 1.31 | 0.308 | N O O O N |
| **Coordination Number 6** | | | | | |
| DETPIB | 1.092 | 1.00 | 0.75 | -0.249 | N N N N N N |
| LEYTAK | 1.032 | 1.00 | 1.42 | 0.423 | N N N N N N |
| SUMFOV | 1.042 | 1.00 | 1.34 | 0.337 | N N N O O O |
| TEJTOR | 1.049 | 1.00 | 0.62 | -0.375 | N N O O O O |
| **Coordination Number 7** | | | | | |
| TODHEZ | 1.064 | 1.00 | 1.45 | 0.450 | N N O O O O O |

Appendix Table B-2 continued.

| REFCODE | Rval | Ox | BVS | Del | Donor Atoms |
|---|---|---|---|---|---|
| **Coordination Number 8** | | | | | |
| CRNASN01 | 1.121 | 1.00 | 0.70 | -0.305 | N N O O O O O O |
| CRNASN01 | 1.121 | 1.00 | 0.90 | -0.099 | N N O O O O O O |
| CRNASN01 | 1.121 | 1.00 | 0.90 | -0.097 | N N O O O O O O |
| CRNASN01 | 1.121 | 1.00 | 0.82 | -0.180 | N N O O O O O O |
| CRSHSB10 | 1.111 | 1.00 | 0.87 | -0.128 | N N O O O O O O |
| CRSHSB10 | 1.111 | 1.00 | 0.73 | -0.272 | N N O O O O O O |
| CRSHSB10 | 1.111 | 1.00 | 0.53 | -0.470 | N N O O O O O O |

Note: REFCODE is the reference code used in the CSD file, Rval is the usual crystallographic *R* value found in the CSD file, Ox is the oxidation state of the Na atom, BVS is the bond valence sum calculated using the $R_0$ value of 1.935 Å. for Na-N, Del is the difference between Ox and BVS. Donor Atoms is the number and type of donor atoms coordinated to the metal cation. Entries where del is > 0.3 valence units are marked with ******

# APPENDIX C
# FORTRAN LINE CODING FOR PROGRAM USED IN CHAPTER 5

Appendix Table C-1. Line coding for FORTRAN program used in Chapter 5.

```
C    BVSCSD08.FOR(Disk BVSUMS-01) 01/09/97 VERSION
C
C    Routine will read the file from QUESTAB1 and calculate the BVS
C    for each entry. The R-zero values are fixed and read in as input.
C    The program asks for the job name or JOBID and uses JOBID.IN as
C    the input file. The files JOBID.OUT and JOBID.SAV are generated
C    by the program. The program will write out at the end a summary
c    of the distances used in the analysis ordered by oxidation state
c    for each type of atom.
C
C    The input is as follows
C
CARD1 TITLE-72A
CARD2 FREE FORMAT--NOTYPE, NOBONDS, BVAL, DIFFO, EXPECT, NEXT
C        NOTYPE is the number of different types of atoms
C        NOBOND is the number of bonds per entry
C        BVAL is usually 0.37
C        DIFFO is the value of the difference between the obs and calc
C            allowed before an entry is flagged
C        EXPECT is the expected or most like valence for each entry
C        NEXT is 0 if no other jobs will be input
c            is > 0 for another job to be read in.
CARDS FORMAT(2X,A2,3X,F7.3)  one for each NOTYPE - atom and Rzero
C
C    The input data to be processed is in the file JOBID.IN.
C
      COMMON /FR/ FLV(40), INV(40), NCHAR, KIN, KFL, KCH, LIN, LOUT
      CHARACTER*72 TITLE
      CHARACTER*12 INPUT, OUTPUT, SAVIT
      CHARACTER*10 CODE
      CHARACTER*8  JOBID, JOBID1, JOBID2, JOBID3
      CHARACTER*6  ENDATA
      CHARACTER*5  ENTRY
      CHARACTER*4  ATM1, ATM2, SAVAT1, BLANK
```

Appendix Table C-1 continued.

```
      CHARACTER*2  ATMSY1, ATMSY2, ATOMS(10), NATM(10)
C
      DIMENSION R0VAL(10), DVAL(5,6), NVAL(5,6), DMIN(5,6), DMAX(5,6)
      DIMENSION BNDVAL(5,6,2000), RINC(10), REND(10), R0DUM(10)
C
      EQUIVALENCE (ATM1, ATMSY1, IATM1(1)), (ATM2, ATMSY2, IATM2(1))
      CHARACTER*1 ISTR(40,8), ICOL(80), IALPU(26), INOS(10),
     1 IATM1(4), IATM2(4),IBLANK, IE, IN, IT
      EQUIVALENCE (INPUT,JOBID1)
      EQUIVALENCE (OUTPUT,JOBID2)
      EQUIVALENCE (SAVIT,JOBID3)
C
      DATA INPUT/'12345678.IN'/
      DATA SAVIT/'12345678.SAV'/
      DATA OUTPUT/'12345678.OUT'/
      DATA ENTRY, ENDATA/'ENTRY','ENDATA'/
      DATA INOS/'1','2','3','4','5','6','7','8','9','0'/
      DATA IBLANK /' '/
      DATA BLANK/'    '/
      DATA IALPU/'A', 'B', 'C', 'D', 'E', 'F', 'G', 'H', 'I', 'J', 'K',
     X 'L', 'M', 'N', 'O', 'P', 'Q', 'R', 'S', 'T', 'U', 'V', 'W', 'X',
     X 'Y', 'Z'/
C
 01   FORMAT(10A1)
 02   FORMAT(A72)
 03   FORMAT(A8)
 04   FORMAT(2X, A5, I6, 5X, A10, 5X, 2F7.3)
 05   FORMAT(5X,2A4,F7.3)
 06   FORMAT(A12)
C 07   FORMAT(2X,A2,3X,F7.3,2X,F7.3,2X,F7.3)
 07   FORMAT(2X,A2,3X,F7.3,F7.3,F7.3)
 08   FORMAT(2X,A10,F6.3,2F7.2,F7.3,' **** ',4X,10(A2,1X))
 09   FORMAT(2X,A10,F6.3,2F7.2,F7.3,10X,10(A2,1X))
 10   FORMAT(' NOTYPE =',I2,'  NOBONDS =',I2, '   BVAL =',F6.3,/
     1 '   DIFFO =',F5.2,'   EXPECT =',F5.1,'   NEXT =',I3/
     2 ' ATOM   RZERO')
 11   FORMAT('  We have reached the end of the data set '/
     1  ' No of entries = ',I5)
 12   FORMAT(2X,A10,F6.3,2F7.2,F7.3,' NOT USED',10(A2,1X))
 15   FORMAT(' PROBLEM WITH ATOM TYPE WE QUIT')
 17   FORMAT(5(5X,A2,F7.3))
C
 16   FORMAT(' SUMMARY OF DISTANCES USED ')
 32   FORMAT(' OUTPUT32.. ',4A1,2X, 4A1,2X, F10.4)
```

Appendix Table C-1 continued.

```
 33  FORMAT(' OUTPUT33.. NEW ATOM IN ENTRY ',2A4, F8.3)
 34  FORMAT(' OUTPUT 34 REFCODE IS ',A8, 5X,' VALENCE = ', F8.3, I5)
 35  FORMAT(' ',A8, 3X,'VAL= ',F6.3,F8.3,4X,I2,2X,15I3/15X,15I3)
 36  FORMAT(20I3)
 38  FORMAT(' SUMDS=',F7.3,'  NUMBER=',I4,'  SIGMA=',F9.5,
    1 '   AVGDEL= ',F7.3)
 39  FORMAT(' ',A8, 3X,'VAL= ',F6.3,F8.3,'*** ',I2,2X,15I3/15X,15I3)
 40  FORMAT(' OUTPUT40.. NEW ATOM IN ENTRY ',2A4, F8.3)
 41  FORMAT(' ...',I3,2X,2(A4,2X),3F10.3)
 42  FORMAT(' OUTPUT42.. ',2(A2,4X),F10.3)
 43  FORMAT(' OUTPUT43.. ',I3,2X, 2(A4,2X), 3F10.3)
 44  FORMAT(' ...', 2(A2,4X),F10.3)
 45  FORMAT(3X,A2,2I6,4F10.3)
 46  FORMAT(' ATOM   VAL   NO',7X,'MIN',7X,'MAX',7X,'AVG',5X,'SIGMA')
 71  FORMAT(' RZER0 VALUE =',F8.3,' ATOM = ',A2,'  VAL =',2F8.3)
 72  FORMAT(' INCTYP=',I5,' R0VAL=',F7.3,' REND=',F7.3,' RINC=',F7.3,
    1 ' SIGMA=',F9.5)
 80  FORMAT(' SUMABS =', F7.3)
C
     DO 200 I1= 1,5
     DO 200 I2 = 1,6
     DVAL(I1,I2) = 0.0
     DMIN(I1,I2) = 9.0
     DMAX(I1,I2) = 0.0
     NVAL(I1,I2) = 0
 200  CONTINUE
     LIN  = 01
     LOUT = 02
     LSAV = 03
     BVAL = 0.37
     VAL = 4.0
     SUMDS = 0.0
     SUMAD = 0.0
     NFUSE = 0.0
     ROUT = 0.7
     SAVAT1 = BLANK
     IMIN = 1
     IMAX = 60
     IDEBUG = 10
     IBOND = 0
     IFINI = 0
     JENT = 0
     NCHAR = 8
     NOUSE = 0
```

Appendix Table C-1 continued.

```
      IE = IALPU(5)
      IN = IALPU(14)
      IT = IALPU(20)
      PRVSGM = 10000.0
C   PrvSgm is the previous sigma
C
 1000 CONTINUE
      WRITE(*, * )  'TYPE IN THE JOB NAME'
      READ (*, 3 ) JOBID
      JOBID1 = JOBID
      JOBID2 = JOBID
      JOBID3 = JOBID
C
      OPEN( 1, FILE=INPUT)
      OPEN( 2, FILE=OUTPUT)
      OPEN( 3, FILE=SAVIT)
      INCTYP = 1
      FRSTRD = 1
C (IncTyp tells us which type (1-NOTYPE) is being incremented in its
C range from RZero to REnd.)
C
250   READ (LIN,  02) TITLE
      WRITE(LOUT, 02) TITLE
      WRITE(LSAV, 02) TITLE
      NOUSE = 0
      SUMDS = 0.0
      SUMABS = 0.0
      SUMAD = 0.0
      READ(LIN, *)  NOTYPE, NBONDS, BVAL, DIFFO, EXPECT, NEXT
      IF(BVAL .LE. 0.01)  BVAL  = 0.37
      IF(DIFFO .LE. 0.01) DIFFO = 0.40
      IF(EXPECT .LE. 0.90) EXPECT = 3.
      WRITE(LOUT, 10) NOTYPE, NBONDS, BVAL, DIFFO, EXPECT, NEXT
      IF(FRSTRD.EQ.0) GO TO 255
      READ (LIN, 07) (NATM(I), R0VAL(I), REND(I), RINC(I), I =1, NOTYPE)
      FRSTRD=0
      GO TO 256
 255  READ (LIN, 07) (NATM(I), R0DUM(I), REND(I), RINC(I), I =1, NOTYPE)
 256  WRITE(LOUT,17) (NATM(I), R0VAL(I), I =1, NOTYPE)
      WRITE(LSAV, 10) NOTYPE, NBONDS, BVAL, DIFFO, EXPECT, NEXT
      WRITE(LSAV,17) (NATM(I), R0VAL(I), I =1, NOTYPE)
C
 100  CONTINUE
      READ (LIN,  04, END=999) ENTRY, ISEQ, CODE, RVAL, VALIN
```

Appendix Table C-1 continued.

```
     WRITE(LOUT, 04) ENTRY, ISEQ, CODE, RVAL, VALIN
      IF(ENTRY .EQ. ENDATA) GO TO 999
      JENT = JENT + 1
      IF(VALIN .LE. 0.90) VALIN = EXPECT
C
      VALSUM = 0.0
      DO 101 I = 1, NBONDS
      CALL READIT(IMIN, IMAX, IDEBUG, IFINI, ISTR, ICOL)
      IF(IFINI .GT. 0) GO TO 999
      DO 54 KO = 1, 4
      IATM1(KO) = ISTR(1, KO)
      IATM2(KO) = ISTR(2, KO)
 54   CONTINUE
      VAL = 0.0
 1542 CONTINUE
      BOND1 = FLV(1)
      DO 542 K1 = 1, 10
      DO 541 K2 = 1,4
      IF(IATM1(K2) .EQ. INOS(K1)) IATM1(K2) = IBLANK
      IF(IATM2(K2) .EQ. INOS(K1)) IATM2(K2) = IBLANK
 541  CONTINUE
 542  CONTINUE
      DO 543 K3 = 1,NOTYPE
      IF(ATMSY2 .EQ. NATM(K3)) GO TO 544
 543  CONTINUE
      WRITE(LOUT, 15)
      STOP
 544  CONTINUE
      IF(RVAL .GE. 1.00) GO TO 2000
      I1 = K3
      I2 = VALIN + 0.1
      IVAL = NVAL(I1,I2) + 1
      NVAL(I1,I2) = IVAL
      IF(IVAL .GT. 2000) GO TO 2000
      BNDVAL(I1,I2,IVAL) = BOND1
      DVAL(I1,I2) = DVAL(I1,I2) + BOND1
      NVAL(I1,I2) = IVAL
      IF(DMIN(I1,I2) .GT. BOND1) DMIN(I1,I2) = BOND1
      IF(DMAX(I1,I2) .LT. BOND1) DMAX(I1,I2) = BOND1
 2000 CONTINUE
      ATOMS(I) = NATM(K3)
      RZER0 = R0VAL(K3)
      DIFF = RZER0 - BOND1
      PART = EXP(DIFF/BVAL)
```

Appendix Table C-1 continued.

```
      VALSUM = VALSUM + PART
      IF(IDEBUG .GT. 0) WRITE(LOUT,71) RZER0, ATOMS(I), VALSUM, PART
 101  CONTINUE
      DIFF  = VALSUM - VALIN
      DIFABS = ABS(DIFF)
      IF(RVAL .GE. 1.00) GO TO 102
      SUMABS = DIFABS + SUMABS
      SUMDS = SUMDS + DIFF**2
      SUMAD = SUMAD + DIFABS
      NOUSE = NOUSE + 1
      IF(DIFFO .LT. DIFABS) WRITE(LSAV,08) CODE, RVAL, VALIN, VALSUM,
     1 DIFF, (ATOMS(I1), I1 = 1,NBONDS)
      IF(DIFFO .GE. DIFABS) WRITE(LSAV,09) CODE, RVAL, VALIN, VALSUM,
     1 DIFF, (ATOMS(I1), I1 = 1,NBONDS)
      GO TO 100
 102  CONTINUE
      WRITE(LSAV,12) CODE, RVAL, VALIN, VALSUM,
     1 DIFF, (ATOMS(I1), I1 = 1,NBONDS)
      GO TO 100
 999  CONTINUE
      WRITE(LOUT, 11) NOUSE
      FUSE = NOUSE
      AVGDEL = SUMAD/FUSE
      FUSE = NOUSE - 1
      SIGMA = SQRT(SUMDS/FUSE)
      WRITE(LOUT, 38) SUMDS, NOUSE, SIGMA, AVGDEL
      WRITE(LSAV, 38) SUMDS, NOUSE, SIGMA, AVGDEL
      WRITE(LSAV, 80) SUMABS
      WRITE(LSAV, 16)
      WRITE(LSAV, 46)

      WRITE(*,72)
INCTYP,R0VAL(INCTYP),REND(INCTYP),RINC(INCTYP),SIGMA

C If sigma begins to rise, go to next type
      IF( SIGMA.GT.PRVSGM ) GO TO 251
      PRVSGM = SIGMA
      R0VAL(INCTYP) = R0VAL(INCTYP) + RINC(INCTYP)
      IF(R0VAL(INCTYP).GT.(REND(INCTYP)+RINC(INCTYP))) GO TO 251

      GO TO 252
251   PRVSGM = 10000
      INCTYP = INCTYP + 1
      IF(INCTYP.GT.NOTYPE) GO TO 253
```

Appendix Table C-1 continued.

```
252   REWIND LIN
      WRITE(LOUT,*)
      WRITE(LSAV,*)
      GO TO 250
253   IF(NEXT .GT. 0) GO TO 1000
      DO 201 I1 = 1,5
      DO 202 I2 = 1,6
      IF(NVAL(I1,I2) .LE. 0) GO TO 202
      IVAL = NVAL(I1,I2)
      FVAL = IVAL
      FVAL2 = FVAL - 1.0
      IF(IVAL .EQ. 1) FVAL2 = 1.0
      AVGD = DVAL(I1,I2)/FVAL
      SUMDIF = 0.0
      SUMD2 = 0.0
      DO 203 I3 = 1, IVAL
      BNDDIF = BNDVAL(I1,I2,I3) - AVGD
      SUMDIF = SUMDIF + ABS(SUMDIF)
      SUMD2 = SUMD2 + BNDDIF**2
      SIGMA = SQRT(SUMD2/FVAL2)
 203  CONTINUE
      WRITE(LSAV, 45) NATM(I1), I2, NVAL(I1,I2),
     X DMIN(I1,I2), DMAX(I1,I2), AVGD, SIGMA
C     WRITE(LSAV, 38) SUMD2, IVAL, SIGMA, AVGDEL
 202  CONTINUE
 201  CONTINUE
      STOP
      END
      SUBROUTINE READIT (IMIN, IMAX, IDEBUG, IFINI, ISTR, ICOL)
      COMMON /FR/ FLV(40), INV(40), NCHAR, KIN, KFL, KCH, LIN, LOUT
      CHARACTER*1 ISTR(40,8), ICOL(80), INUM(10), ICH,
     1 IBLANK, IPLUS, IMINUS, IPOINT
      DATA INUM/'1','2','3','4','5','6','7','8','9','0'/
      DATA IBLANK, IPLUS,  IMINUS/' ','+','-'/
      DATA IPOINT /'.'/
   10 FORMAT(80A1)
   20 FORMAT(5X,80A1)
      READ (LIN, 10, END = 999) (ICOL(I1), I1 = 1, IMAX)
      IF(IDEBUG .GT. 0) WRITE(LOUT,20) (ICOL(I1), I1 = 1, IMAX)
      DO 2601 JZ = 1,40
      FLV(JZ) = 0.0
      INV(JZ) = 0
      DO 2604 JY = 1 ,8
      ISTR(JZ,JY) = IBLANK
```

Appendix Table C-1 continued.

```
 2604 CONTINUE
 2601 CONTINUE
     KIN = 0
     KFL = 0
     KCH = 0
     I=IMIN-1
C
C**** START OF A NEW FIELD
C**** LOOK FOR A NON-BLANK COLUMN
C
  109 CONTINUE
     IA = 0
     IP = 0
     NP = 0
     L = 0
     ISGN = 1
  110 CONTINUE
     I=I+1
     IF(I.GT.IMAX)  GO TO 108
  111 CONTINUE
     ICH = ICOL(I)
     IF(L.EQ.0  .AND.  ICH.EQ.IBLANK)  GO TO 110
C**** START OF A FIELD
     L=L+1
     DO 100 J=1,10
     IF(ICH.EQ.INUM(J)) GO TO 101
  100 CONTINUE
     IF(ICH.EQ.IPOINT)  GO TO 102
     IF(ICH.EQ.IPLUS)  GO TO 103
     IF(ICH.EQ.IMINUS)  GO TO 104
     IF(L.GT.1)  GO TO 105
     GO TO 150
C
C**** START OF A LITERAL FIELD BY A CHARACTER WHICH IS OTHE9 THA5
0 9+ .
C
C**** NUMERIC FIELD FOUND
C
  101 IF(J.EQ.10)  J=0
     IF(IP.EQ.1)  NP=NP+1
  106 CONTINUE
     IA = 10*IA + J
     GO TO 110
  102 IP=1
```

Appendix Table C-1 continued.

```
      GO TO 110
  103 IF(L.GT.1)  GO TO 105
      ISGN = 1
      GO TO 110
  104 IF(L.GT.1)  GO TO 105
      ISGN = -1
      GO TO 110
  108 IF(L.GT.0)  GO TO 105
      GO TO 120
C
C**** END OF NUMERIC FIELD
C
  105 CONTINUE
      IF(IP.EQ.0) GO TO 1050
      IF(IA.EQ.0) GO TO 1060
      A = ISGN*IA
      A = A/10.0**NP
 1061 CONTINUE
      KFL = KFL + 1
      FLV(KFL) = A
      IF(ICH .EQ. IBLANK) GO TO 109
      I = I - 1
      GO TO 109
 1060 CONTINUE
      A = 0.0
      GO TO 1061
 1050 CONTINUE
      KIN = KIN + 1
      IA = ISGN*IA
      INV(KIN) = IA
      IF(ICH .EQ. IBLANK) GO TO 109
      I = I - 1
      GO TO 109
C
C**** LITERAL FIELD
C
  150 CONTINUE
      IF(KCH.GE.10) GO TO 109
      KCH = KCH + 1
  151 CONTINUE
      IF(L.GT.NCHAR)  GO TO 109
      ISTR(KCH,L) = ICH
      I = I + 1
      IF(I .GT. IMAX) GO TO 120
```

Appendix Table C-1 continued.

```
      ICH = ICOL(I)
      IF(ICH.EQ.IBLANK)  GO TO 152
      L = L + 1
      GO TO 151
C
C**** END OF LITERAL FIELD DEFINED BY BLANK
C
  152 CONTINUE
      GO TO 109
C
C**** FINISHED
C
  120 RETURN
  999 WRITE(LOUT, 998)
  998 FORMAT(' *****WE ARE FINISHED IN READIT*****')
      IFINI = 10
      RETURN
      END
```

# APPENDIX D
# TABLES OF CRYSTALLOGRAPHIC DATA

Appendix Table D-1. Crystallographic data for Ni(2-acetylpyridine thiosemicarbazone)$_2$

## A. Crystal data (143(2) K)

| | |
|---|---|
| $a$, Å | 16.94300(10) |
| $b$, Å | 13.7203(2) |
| $c$, Å | 23.5334(3) |
| $\alpha$, deg. | 90 |
| $\beta$, deg. | 109.6810(10) |
| $\gamma$, deg | 90 |
| V, Å$^3$ | 5151.06(10) |
| $d_{\mathrm{calc}}$, Mg m$^{-3}$ | 1.566 |
| Empirical formula | C16 H24 N10 Ni O8 S2 |
| Formula weight, g | 607.28 |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Z | 8 |
| F(000), electrons | 2512 |
| Crystal size (mm$^3$) | 0.24 x 0.22 x 0.19 |

## B. Data Collection

| | |
|---|---|
| Absorption coefficient | 0.977 mm$^{-1}$ |
| Theta range for data collection | 1.75 to 27.50 deg. |
| Limiting indices | $-20\leq h\leq 22$, $-17\leq k\leq 15$, $-30\leq l\leq 30$ |
| Reflections collected | 32553 |
| Independent reflections | 11771 [R(int) = 0.0283] |
| Completeness to theta = 27.50° | 99.5% |
| Max. and min. transmission | 0.8414 and 0.7810 |
| Absorption correction | Integration |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 11771 / 0 / 860 |

Appendix Table D-1 continued.

### C. Structure refinement

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.003 |
| Final R indices $[I>2\sigma(I)]$ | R1 = 0.0281, wR2 = 0.0686 [8992] |
| R indices (all data) | R1 = 0.0442, wR2 = 0.0720 |
| Extinction coefficient | 0.00032(6) |
| Largest diff. Peak and hole | 0.396 and –0.302 e.$Å^3$ |

Appendix Table D-2. Bond lengths [Å] and angles [°] for Ni(2-acetylpyridine thiosemicarbazone)$_2$.

| | |
|---|---|
| Ni1-N2 | 2.0242(13) |
| Ni1-N12 | 2.0312(13) |
| Ni1-N1 | 2.0824(14) |
| Ni1-N11 | 2.0922(13) |
| Ni1-S1 | 2.4128(4) |
| Ni1-S11 | 2.4162(4) |
| S1-C9 | 1.6966(16) |
| N1-C6 | 1.345(2) |
| N1-C2 | 1.358(2) |
| N2-C7 | 1.296(2) |
| N2-N3 | 1.3697(19) |
| N3-C9 | 1.365(2) |
| N3-H3A | 0.81(2) |
| N4-C9 | 1.317(2) |
| N4-H4A | 0.89(2) |
| N4-H4B | 0.87(2) |
| S11-C19 | 1.6983(17) |
| N11-C16 | 1.340(2) |
| N11-C12 | 1.356(2) |
| N12-C17 | 1.297(2) |
| N12-N13 | 1.3678(18) |
| N13-C19 | 1.365(2) |
| N13-H13A | 0.860(19) |
| N14-C19 | 1.328(2) |
| N14-H14A | 0.84(2) |
| N14-H14B | 0.88(2) |

| | |
|---|---|
| N2-Ni1-N12 | 171.26(5) |
| N2-Ni1-N1 | 78.09(5) |
| N12-Ni1-N1 | 98.05(5) |
| N2-Ni1-N11 | 94.14(5) |
| N12-Ni1-N11 | 78.13(5) |
| N1-Ni1-N11 | 93.03(5) |
| N2-Ni1-S1 | 82.39(4) |
| N12-Ni1-S1 | 160.37(4) |
| N11-Ni1-S1 | 90.43(4) |
| N2-Ni1-S11 | 104.85(4) |
| N12-Ni1-S11 | 82.81(4) |
| N1-Ni1-S11 | 89.34(4) |
| N11-Ni1-S11 | 160.94(4) |
| S1-Ni1-S11 | 93.661(16) |

Appendix Table D-1 continued.

| | |
|---|---|
| C9-S1-Ni1 | 96.12(6) |
| C6-N1-C2 | 118.51(15) |
| C6-N1-Ni1 | 127.36(12) |
| C2-N1-Ni1 | 113.44(11) |
| C7-N2-N3 | 120.33(14) |
| C7-N2-Ni1 | 118.37(11) |
| N3-N2-Ni1 | 120.14(10) |
| C9-N3-N2 | 118.59(14) |
| C9-N3-H3A | 117.4(15) |
| N2-N3-H3A | 121.7(15) |
| C9-N4-H4A | 118.6(14) |
| C9-N4-H4B | 119.0(14) |
| H4A-N4-H4B | 122.4(19) |
| N1-C2-C3 | 121.97(17) |
| N1-C2-C7 | 115.06(14) |
| N1-C6-C5 | 122.24(19) |
| N1-C6-H6 | 115.8(11) |
| N2-C7-C2 | 113.61(15) |
| N2-C7-C8 | 124.68(17) |

Appendix Table D-3. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for Ni(2-acetylpyridine thiosemicarbazone)$_2$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ni1 | 3610(1) | -384(1) | 2461(1) | 20(1) |
| S1 | 2790(1) | -1699(1) | 1870(1) | 25(1) |
| N1 | 4058(1) | 1018(1) | 2720(1) | 25(1) |
| N2 | 2990(1) | 400(1) | 1716(1) | 23(1) |
| N3 | 2485(1) | -60(1) | 1207(1) | 27(1) |
| N4 | 1821(1) | -1426(1) | 738(1) | 35(1) |
| C2 | 3732(1) | 1698(1) | 2284(1) | 27(1) |
| C3 | 3859(1) | 2691(1) | 2397(1) | 35(1) |
| C4 | 4324(1) | 2986(2) | 2980(1) | 42(1) |
| C5 | 4664(1) | 2302(2) | 3418(1) | 38(1) |
| C6 | 4524(1) | 1322(1) | 3275(1) | 31(1) |
| C7 | 3196(1) | 1305(1) | 1694(1) | 26(1) |
| C8 | 2941(2) | 1914(2) | 1137(1) | 41(1) |
| C9 | 2338(1) | -1033(1) | 1236(1) | 25(1) |
| S11 | 2756(1) | -258(1) | 3100(1) | 25(1) |
| N11 | 4606(1) | -733(1) | 2162(1) | 23(1) |
| N12 | 4392(1) | -1114(1) | 3183(1) | 21(1) |
| N13 | 4168(1) | -1258(1) | 3683(1) | 23(1) |
| N14 | 3277(1) | -1001(1) | 4205(1) | 28(1) |
| C12 | 5226(1) | -1236(1) | 2576(1) | 23(1) |
| C13 | 5930(1) | -1561(1) | 2451(1) | 28(1) |
| C14 | 5987(1) | -1375(1) | 1885(1) | 32(1) |
| C15 | 5359(1) | -866(1) | 1466(1) | 32(1) |
| C16 | 4675(1) | -553(1) | 1622(1) | 27(1) |
| C17 | 5102(1) | -1436(1) | 3162(1) | 23(1) |
| C18 | 5748(1) | -1981(1) | 3646(1) | 30(1) |
| C19 | 3432(1) | -867(1) | 3693(1) | 23(1) |

Appendix Table D-3 continued.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ni2 | 3559(1) | 4891(1) | -2621(1) | 21(1) |
| S21 | 2764(1) | 3541(1) | -3198(1) | 26(1) |
| N21 | 3965(1) | 6323(1) | -2407(1) | 26(1) |
| N22 | 2972(1) | 5617(1) | -3411(1) | 24(1) |
| N23 | 2521(1) | 5110(1) | -3915(1) | 29(1) |
| N24 | 1942(1) | 3702(1) | -4372(1) | 42(1) |
| C22 | 3656(1) | 6962(1) | -2872(1) | 27(1) |
| C23 | 3764(1) | 7963(1) | -2788(1) | 35(1) |
| C24 | 4184(1) | 8310(2) | -2214(1) | 43(1) |
| C25 | 4499(1) | 7668(2) | -1745(1) | 42(1) |
| C26 | 4381(1) | 6672(1) | -1858(1) | 34(1) |
| C27 | 3170(1) | 6518(1) | -3458(1) | 27(1) |
| C28 | 2950(2) | 7066(2) | -4042(1) | 38(1) |
| C29 | 2387(1) | 4141(1) | -3864(1) | 28(1) |
| S31 | 2647(1) | 5047(1) | -2032(1) | 26(1) |
| N31 | 4611(1) | 4515(1) | -2852(1) | 23(1) |
| N32 | 4322(1) | 4227(1) | -1854(1) | 21(1) |
| N33 | 4060(1) | 4124(1) | -1367(1) | 23(1) |
| N34 | 3073(1) | 4356(1) | -924(1) | 29(1) |
| C32 | 5223(1) | 4061(1) | -2404(1) | 22(1) |
| C33 | 5961(1) | 3748(1) | -2481(1) | 28(1) |
| C34 | 6060(1) | 3880(1) | -3040(1) | 32(1) |
| C35 | 5433(1) | 4327(1) | -3497(1) | 32(1) |
| C36 | 4721(1) | 4641(1) | -3383(1) | 26(1) |
| C37 | 5049(1) | 3900(1) | -1834(1) | 22(1) |
| C38 | 5660(1) | 3377(2) | -1316(1) | 31(1) |
| C39 | 3292(1) | 4485(1) | -1407(1) | 23(1) |
| N40 | 1322(1) | 5063(1) | -551(1) | 28(1) |
| O41 | 1961(1) | 5483(1) | -189(1) | 34(1) |
| O42 | 641(1) | 5092(1) | -461(1) | 39(1) |
| O43 | 1382(1) | 4637(1) | -1006(1) | 42(1) |

Appendix Table D-3 continued.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N50 | 864(1) | 723(1) | -98(1) | 34(1) |
| O51 | 251(1) | 1117(1) | -474(1) | 56(1) |
| O52 | 1188(1) | -24(1) | -228(1) | 64(1) |
| O53 | 1174(1) | 1088(1) | 414(1) | 43(1) |
| N60 | 4114(1) | 993(1) | 112(1) | 42(1) |
| O61 | 4761(1) | 1031(2) | 550(1) | 84(1) |
| O62 | 4029(1) | 1477(1) | -351(1) | 45(1) |
| O63 | 3510(1) | 465(1) | 129(1) | 59(1) |
| N70 | 3751(1) | 4166(1) | 642(1) | 30(1) |
| O71 | 4421(1) | 4506(1) | 593(1) | 40(1) |
| O72 | 3527(1) | 4424(1) | 1072(1) | 42(1) |
| O73 | 3324(1) | 3573(1) | 262(1) | 37(1) |
| O10 | -1499(1) | 3491(1) | -678(1) | 37(1) |
| O20 | 148(1) | 2983(1) | 153(1) | 38(1) |
| O30 | 4884(1) | 3333(1) | -195(1) | 33(1) |
| O40 | 6686(1) | 3274(1) | 362(1) | 60(1) |

Note: U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

Appendix Table D-4. Anisotropic displacement parameters (Å$^2$x 10$^3$)for Ni(2-acetylpyridine thiosemicarbazone)$_2$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ni1 | 21(1) | 19(1) | 22(1) | 1(1) | 8(1) | 0(1) |
| S1 | 26(1) | 20(1) | 25(1) | 2(1) | 5(1) | 0(1) |
| N1 | 23(1) | 24(1) | 30(1) | -2(1) | 13(1) | -2(1) |
| N2 | 24(1) | 21(1) | 25(1) | 1(1) | 1_(1) | 1(1) |
| N3 | 30(1) | 22(1) | 23(1) | 4(1) | 2(1) | 2(1) |
| N4 | 42(1) | 25(1) | 29(1) | 1(1) | -2(1) | -1(1) |
| C2 | 24(1) | 22(1) | 40(1) | -2(1) | 19(1) | -1(1) |
| C3 | 30(1) | 24(1) | 57(1) | -1(1) | 21(1) | 0(1) |
| C4 | 38(1) | 26(1) | 68(2) | -19(1) | 27(1) | -11(1) |
| C5 | 34(1) | 40(1) | 46(1) | -19(1) | 20(1) | -12(1) |
| C6 | 29(1) | 35(1) | 31(1) | -7(1) | 15(1) | -7(1) |
| C7 | 25(1) | 21(1) | 36(1) | 5(1) | 14(1) | 2(1) |
| C8 | 50(1) | 27(1) | 44(1) | 14(1) | 10(1) | -4(1) |
| C9 | 25(1) | 23(1) | 26(1) | 1(1) | 8(1) | 3(1) |
| S11 | 22(1) | 28(1) | 27(1) | 2(1) | 10(1) | 2(1) |
| N11 | 23(1) | 22(1) | 25(1) | -3(1) | 1_(1) | -2(1) |
| N12 | 22(1) | 20(1) | 22(1) | -1(1) | 8(1) | -1(1) |
| N13 | 23(1) | 25(1) | 21(1) | 2(1) | 8(1) | 2(1) |
| N14 | 28(1) | 32(1) | 28(1) | 1(1) | 14(1) | 1(1) |
| C12 | 23(1) | 19(1) | 28(1) | -5(1) | 9(1) | -4(1) |
| C13 | 23(1) | 27(1) | 36(1) | -2(1) | 12(1) | 0(1) |
| C14 | 29(1) | 33(1) | 41(1) | -7(1) | 21(1) | -2(1) |
| C15 | 37(1) | 33(1) | 32(1) | -4(1) | 19(1) | -6(1) |
| C16 | 29(1) | 27(1) | 27(1) | -1(1) | 11(1) | -4(1) |
| C17 | 24(1) | 18(1) | 26(1) | -3(1) | 7(1) | -2(1) |
| C18 | 28(1) | 31(1) | 28(1) | -1(1) | 8(1) | 7(1) |
| C19 | 25(1) | 20(1) | 26(1) | -3(1) | 11(1) | -4(1) |
| Ni2 | 21(1) | 20(1) | 21(1) | 1(1) | 8(1) | 1(1) |
| S21 | 26(1) | 22(1) | 28(1) | 1(1) | 7(1) | 0(1) |
| N21 | 26(1) | 25(1) | 31(1) | -2(1) | 12(1) | -2(1) |
| N22 | 25(1) | 22(1) | 24(1) | 0(1) | 7(1) | 3(1) |
| N23 | 35(1) | 27(1) | 22(1) | 4(1) | 4(1) | 4(1) |
| N24 | 50(1) | 32(1) | 31(1) | -4(1) | -5(1) | 3(1) |
| C22 | 25(1) | 23(1) | 39(1) | 0(1) | 17(1) | 1(1) |
| C23 | 31(1) | 24(1) | 54(1) | -1(1) | 19(1) | 0(1) |
| C24 | 36(1) | 27(1) | 70(2) | -13(1) | 22(1) | -5(1) |

Appendix Table D-4 continued.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C25 | 34(1) | 43(1) | 48(1) | -20(1) | 14(1) | -11(1) |
| C26 | 30(1) | 36(1) | 35(1) | -8(1) | 12(1) | -6(1) |
| C27 | 28(1) | 23(1) | 32(1) | 5(1) | 14(1) | 5(1) |
| C28 | 45(1) | 30(1) | 38(1) | 11(1) | 14(1) | 2(1) |
| C29 | 26(1) | 26(1) | 29(1) | -2(1) | 6(1) | 4(1) |
| S31 | 22(1) | 30(1) | 26(1) | 4(1) | 9(1) | 5(1) |
| N31 | 24(1) | 22(1) | 24(1) | -2(1) | 10(1) | -2(1) |
| N32 | 22(1) | 22(1) | 21(1) | 0(1) | 8(1) | -1(1) |
| N33 | 22(1) | 28(1) | 20(1) | 4(1) | 9(1) | 3(1) |
| N34 | 25(1) | 38(1) | 26(1) | 5(1) | 13(1) | 6(1) |
| C32 | 23(1) | 20(1) | 25(1) | -1(1) | 9(1) | -2(1) |
| C33 | 26(1) | 27(1) | 35(1) | 2(1) | 13(1) | 0(1) |
| C34 | 30(1) | 33(1) | 42(1) | -2(1) | 22(1) | 1(1) |
| C35 | 36(1) | 34(1) | 31(1) | -3(1) | 19(1) | -4(1) |
| C36 | 30(1) | 28(1) | 22(1) | 2(1) | 1_(1) | -1(1) |
| C37 | 22(1) | 20(1) | 24(1) | -1(1) | 7(1) | 0(1) |
| C38 | 25(1) | 37(1) | 29(1) | 4(1) | 1_(1) | 9(1) |
| C39 | 23(1) | 22(1) | 25(1) | 0(1) | 9(1) | 0(1) |
| N40 | 28(1) | 27(1) | 31(1) | 3(1) | 12(1) | 4(1) |
| O41 | 31(1) | 38(1) | 34(1) | -4(1) | 12(1) | -4(1) |
| O42 | 27(1) | 53(1) | 43(1) | -3(1) | 19(1) | 1(1) |
| O43 | 34(1) | 56(1) | 40(1) | -18(1) | 16(1) | 2(1) |
| N50 | 40(1) | 35(1) | 28(1) | 8(1) | 11(1) | 7(1) |
| O51 | 58(1) | 46(1) | 44(1) | 4(1) | -1_(1) | 19(1) |
| O52 | 101(1) | 57(1) | 32(1) | 1_(1) | 19(1) | 44(1) |
| O53 | 51(1) | 45(1) | 27(1) | 3(1) | 6(1) | 4(1) |
| N60 | 54(1) | 41(1) | 27(1) | -10(1) | 8(1) | -12(1) |
| O61 | 87(1) | 86(1) | 46(1) | -3(1) | -21(1) | -31(1) |
| O62 | 56(1) | 49(1) | 34(1) | 2(1) | 21(1) | 2(1) |
| O63 | 82(1) | 55(1) | 44(1) | -14(1) | 27(1) | -34(1) |
| N70 | 33(1) | 30(1) | 30(1) | 4(1) | 15(1) | 2(1) |
| O71 | 33(1) | 49(1) | 44(1) | -5(1) | 22(1) | -1_(1) |
| O72 | 48(1) | 50(1) | 42(1) | -11(1) | 30(1) | -1_(1) |
| O73 | 42(1) | 39(1) | 30(1) | -2(1) | 13(1) | -11(1) |
| O10 | 50(1) | 28(1) | 35(1) | -4(1) | 17(1) | 0(1) |
| O20 | 44(1) | 32(1) | 34(1) | -8(1) | 8(1) | 5(1) |
| O30 | 35(1) | 38(1) | 31(1) | 6(1) | 16(1) | 5(1) |
| O40 | 36(1) | 42(1) | 88(1) | 23(1) | 3(1) | 0(1) |

Note: The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U^{11} + \ldots + 2\, h\, k\, a^{*}\, b^{*}\, U^{12}\, ]$

Appendix Table D-5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for Ni(2-acetylpyridine thiosemicarbazone)$_2$.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H3A | 2171(13) | 243(15) | 923(9) | 39(6) |
| H4A | 1740(13) | -2069(17) | 728(9) | 47(6) |
| H4B | 1591(13) | -1053(16) | 426(10) | 47(6) |
| H3 | 3635(11) | 3147(14) | 2097(8) | 32(5) |
| H4 | 4389(12) | 3637(16) | 3059(9) | 40(6) |
| H5 | 4986(13) | 2469(16) | 3822(10) | 51(6) |
| H6 | 4727(11) | 827(14) | 3568(8) | 29(5) |
| H8A | 2387(16) | 2133(18) | 1040(10) | 63(8) |
| H8B | 3302(15) | 2455(18) | 1174(10) | 63(7) |
| H8C | 2941(13) | 1520(17) | 782(10) | 57(7) |
| H13A | 4503(11) | -1533(14) | 4001(8) | 30(5) |
| H14A | 2812(13) | -804(15) | 4214(9) | 36(6) |
| H14B | 3647(13) | -1303(16) | 4512(9) | 46(6) |
| H13 | 6341(11) | -1892(14) | 2744(8) | 34(5) |
| H14 | 6476(12) | -1604(14) | 1809(8) | 32(5) |
| H15 | 5352(12) | -697(14) | 1087(9) | 35(5) |
| H16 | 4247(12) | -181(13) | 1349(8) | 30(5) |
| H18A | 5594(13) | -2094(15) | 4005(10) | 46(6) |
| H18B | 6259(15) | -1685(18) | 3736(10) | 57(7) |
| H18C | 5825(13) | -2586(17) | 3505(9) | 46(6) |
| H23A | 2241(13) | 5394(15) | -4232(10) | 45(6) |
| H24A | 1857(14) | 3060(19) | -4391(10) | 54(7) |
| H24B | 1681(16) | 4040(19) | -4657(11) | 70(9) |
| H23 | 3535(13) | 8378(16) | -3104(10) | 50(6) |
| H24 | 4252(12) | 8971(16) | -2138(9) | 44(6) |
| H25 | 4785(13) | 7857(16) | -1367(10) | 50(6) |
| H26 | 4580(10) | 6176(13) | -1550(8) | 23(4) |
| H28A | 3036(15) | 6634(19) | -4364(11) | 71(8) |
| H28B | 2355(15) | 7204(17) | -4195(10) | 59(7) |
| H28C | 3248(15) | 7651(18) | -4008(11) | 67(8) |
| H33A | 4385(12) | 3908(15) | -1019(9) | 41(6) |
| H34A | 2596(13) | 4538(14) | -944(9) | 37(6) |
| H34B | 3396(13) | 4061(15) | -588(10) | 45(6) |
| H33 | 6361(12) | 3469(15) | -2165(9) | 39(6) |
| H34 | 6568(13) | 3651(15) | -3084(9) | 44(6) |
| H35 | 5469(12) | 4423(15) | -3868(9) | 40(6) |
| H36 | 4306(11) | 4930(13) | -3678(8) | 22(4) |
| H38A | 5406(15) | 3098(19) | -1037(11) | 73(8) |
| H38B | 6130(20) | 3790(30) | -1158(15) | 130(13) |

Appendix Table D-5 continued.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H38C | 5916(15) | 2892(19) | -1441(11) | 66(8) |
| H12 | -1703(16) | 3740(20) | -1029(12) | 77(9) |
| H11 | -1661(16) | 3850(20) | -457(12) | 73(9) |
| H22 | 220(14) | 2455(18) | 45(10) | 55(8) |
| H21 | -259(17) | 3250(20) | -105(12) | 73(9) |
| H32 | 4708(13) | 2764(18) | -167(9) | 46(7) |
| H31 | 4762(15) | 3671(19) | 56(11) | 65(8) |
| H42 | 6977(17) | 3670(20) | 341(12) | 74(10) |
| H41 | 6190(17) | 3430(19) | 199(12) | 71(9) |

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# BIOGRAPHICAL SKETCH

Richard Malcolm Wood was born in Bangor, Maine, on August 30, 1973, to Roderick and Jung Ja Wood. After graduating from Castle High School of Newburgh, Indiana, in 1991, he attended the University of Evansville (Indiana) and majored in chemistry until 1995 when he obtained a Bachelor of Science in chemistry. He then came to Gainesville, Florida, to pursue graduate studies in chemistry in 1995 under Dr. Gus Palenik. Upon completion of his doctorate, Mr. Wood plans to move to the Midwest with his family. Mr. Wood is married and he and his wife are expecting their first child in early September, 2000.

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This thesis was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 2000

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